

# Supporting Information

## Unveiling the Takai Olefination Reagent via Tris(*tert*-butoxy)siloxy Variants

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# Table of Contents

<b>Experimental</b> .....	<b>S3</b>
General.....	S3
Synthesis of precursors and organochromium reagents .....	S3
Reactions with TMEDA.....	S6
Test and blank reactions.....	S7
Reactions of the organochromium reagents with either benzaldehyde or 4- <i>tert</i> -butylcyclohexanone.....	S7
Preliminary reactions between organochromium reagents and allyl benzyl ether .....	S9
<b>X-Ray Crystallography</b> .....	<b>S10</b>
Table S1. X-ray crystallographic parameters for complexes <b>2-10</b> .....	S10-11
<b>Supplementary Figures and Schemes Associated with the Manuscript (Figures S1-S14)</b> .....	<b>S12</b>
Figure S1. Connectivity structure of $[\text{Cr}_2\text{Cl}_4(\text{CHI})(\text{thf})_4]$ ( <b>1</b> ), along with provided bond lengths.....	S12
Figure S2. $^2\text{D}$ NMR spectrum of $[\text{Cr}_2\text{Cl}_4(\text{CDI})(\text{thf})_{3.5}]$ ( <b>1<sup>D</sup></b> ) in THF .....	S12
Figure S3. Crystal structure of $[\text{CrCl}_2\text{I}(\text{thf})_3]$ ( <b>2</b> ) .....	S13
Scheme S1. Likely formation of Cr–I species through decomposition of an Cr– $\text{CHI}_2$ intermediate .....	S13
Figure S4. Crystal structure of $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2\text{I}(\text{thf})_3]$ ( <b>4</b> ) .....	S14
Figure S5. $^1\text{H}$ NMR spectrum of $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2]$ with half an equivalent of $\text{CHI}_3$ .....	S15
Figure S6. Crystal structure of $[\text{Cr}_2\text{I}(\text{OSi}(\text{O}t\text{Bu})_3)_4]$ ( <b>6a</b> ). .....	S16
Figure S7. Crystal structure of $[\text{CrCl}_2(\text{tmeda})_2][\text{I}]\cdot\text{THF}$ ( <b>7</b> ).....	S17
Figure S8. Stacked $^2\text{D}$ NMR spectra of $[\text{Cr}_2\text{Cl}_4(\text{CDI})(\text{thf})_{3.5}]$ ( <b>1</b> ) with TMEDA in THF .....	S18
Figure S9. Crystal structure of $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{tmeda})]$ ( <b>8</b> ) .....	S19
Figure S10. Stacked $^1\text{H}$ NMR spectra of $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{tmeda})]$ ( <b>8</b> ) and its reaction with $\text{CHI}_3$ . .....	S20
Figure S11. Crystal structure of $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{tmeda})]$ ( <b>10</b> ).....	S21
Figure S12. $^1\text{H}$ NMR spectra of <i>in situ</i> generated <b>9</b> and benzaldehyde .....	S22
Figure S13. $^1\text{H}$ NMR spectrum of $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2]$ and benzaldehyde .....	S22
Figure S14. Connectivity structure of $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2\text{I}(\text{benzaldehyde})]\cdot\text{C}_6\text{D}_6$ ( <b>11</b> ).....	S23
<b>Additional Relevant Spectra</b> .....	<b>S24</b>
Figure S15. $^1\text{H}$ NMR spectrum of the reaction between $\text{CrCl}_2$ , iodoform, and benzaldehyde .....	S24
Figure S16. $^1\text{H}$ NMR spectrum of the reaction between <b>1</b> and half an equivalent of benzaldehyde, .....	S25
Figure S17. $^1\text{H}$ NMR spectrum of <i>in situ</i> generated <b>5a</b> and half an equivalent of benzaldehyde .....	S26
Figure S18. $^1\text{H}$ NMR spectrum of <b>1</b> and one an equivalent of 4- <i>tert</i> -butylcyclohexanone .....	S27
Figure S19. $^1\text{H}$ NMR spectrum of <i>in situ</i> generated <b>5a</b> and 4- <i>tert</i> -butylcyclohexanone .....	S28
Figure S20. $^1\text{H}$ NMR spectrum of <i>in situ</i> generated <b>9</b> and 4- <i>tert</i> -butylcyclohexanone.. .....	S29
Figure S21. $^2\text{D}$ NMR spectrum of <b>1<sup>D</sup></b> with two equivalents of TMEDA and one equivalent of allyl benzyl ether .....	S30
<b>References</b> .....	<b>S31</b>

## Experimental

**General.** All manipulations were performed using glovebox (MBraun 200B; <0.1 ppm O<sub>2</sub>, <0.1 ppm H<sub>2</sub>O), or Schlenk line techniques under an atmosphere of purified argon in oven dried glassware. Solvents (THF, *n*-hexane, and toluene) were purified by Grubbs columns (MBraun SPS, solvent purification system), and stored in a glovebox. THF was further dried over NaK, distilled under argon, and freshly degassed before use. Chromium(II) chloride was purchased from Sigma Aldrich (99.99% pure, trace metal basis), and used as received. TMEDA was purchased from Sigma Aldrich, and dried over molecular sieves. Iodoform was purchased from Sigma-Aldrich, and sublimed before use. CDI<sub>3</sub> and HOSi(*O**t*Bu)<sub>3</sub> were purchased from Sigma-Aldrich and used as received. [Cr(OSi(*O**t*Bu)<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was synthesized according to a literature procedure.<sup>1</sup> Benzaldehyde, and benzyl allyl ether were each purchased from Sigma-Aldrich, and were dried over pre-dried 3 Å molecular sieves, and further purified by distillation. 4-*tert*-Butyl-cyclohexanone was purchased from Sigma-Aldrich and was purified by sublimation prior to use. The NMR spectra of air and moisture-sensitive compounds were performed in pre-dried (over NaK) benzene-d<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>), or THF-d<sub>8</sub> (further purified by distillation), with J. Young valve NMR spectroscopy tubes. Analyses were performed at 300 K with a Bruker AVII+400 (<sup>1</sup>H: 400.13 MHz, <sup>13</sup>C: 100.16 MHz), and where specified either a Bruker-Avance II 500 (<sup>1</sup>H: 500.13 MHz; <sup>2</sup>D: 76.77 MHz, <sup>13</sup>C: 125.77 MHz), or a Bruker DRX250 (<sup>1</sup>H: 250 MHz, <sup>13</sup>C 63 MHz) machine. Infrared spectra were recorded on a Nicolet 6700 FTIR spectrometer ( $\tilde{\nu}$  = 4000-600 cm<sup>-1</sup>), using a DRIFT chamber with dry KBr/sample mixtures and KBr windows. Samples for elemental analysis (C, H, N) were taken from the bulk material, and were analysed on an Elementar Vario Micro cube. Magnetic susceptibilities and  $\mu_{\text{eff}}$  were calculated by the Evans method.<sup>2,3</sup> <sup>1</sup>H NMR measurements were performed with a scan range of both 20 ppm (-5 – 15 ppm) and 200 ppm (-100 – 100 ppm), however, as there were no resonances observed below – 5 ppm and beyond 15 ppm, the wide-range NMR spectra are not presented.

### Synthesis of precursors and organochromium reagents.

**[Cr<sub>2</sub>Cl<sub>4</sub>(CHI)(thf)<sub>x</sub>] (1, x = 4 or 3.5), [CrCl<sub>2</sub>I(thf)<sub>3</sub>] (2), and [Cr<sub>2</sub>Cl<sub>2</sub>(OSi(*O**t*Bu)<sub>3</sub>)<sub>2</sub>(CHI)(thf)<sub>4</sub>] (3):** CrCl<sub>2</sub> (0.165 g, 1.3 mmol, four equiv) was stirred in THF (2-3 mL) at ambient temperature, giving a pale blue/pale green slurry. The mixture was then cooled to -35 °C, and a cold (-35 °C) THF solution of iodoform (0.133 g, 0.34 mmol, one equiv) was slowly added dropwise at -35 °C. Upon slowly warming to ambient temperature (over the course of half an hour), the solution turned deep red, and an orange precipitate formed (later identified as [CrCl<sub>2</sub>I(thf)<sub>3</sub>] (2)). After filtration from **2**, the light red solution was concentrated and stored at -35 °C, giving red crystals and a red supernatant solution. The crystals diffracted poorly, despite suitable size, but gave the overall connectivity of [Cr<sub>2</sub>Cl<sub>4</sub>(CHI)(thf)<sub>4</sub>] (**1**, see Figure S1). One set of crystals contained one unit in the asymmetric unit:  $a = 10.83(5)$  Å,  $b = 17.19(8)$  Å,  $c = 13.61(6)$  Å,  $\beta = 90.19(8)$  °; one set contained three units within the asymmetric unit:  $a = 17.269(2)$  Å,  $b = 41.0444(4)$  Å,  $c = 10.940(1)$  Å,  $\alpha = \beta = \gamma = 90$ °. Upon drying *in vacuo*, partial loss of THF was observed giving a red amorphous powder of [Cr<sub>2</sub>Cl<sub>4</sub>(CHI)(thf)<sub>3.5</sub>] (**1**). Yield: 0.10 g (47%, dried crystal yield). DRIFT:  $\nu = 2971$  (w), 2895 (w), 1615 (present only upon air exposure), 1470 (vw), 1456 (w), 1447 (w), 1345 (vw), 1296 (vw), 1245 (w), 1175 (vw), 1021 (s), 1014 (s), 957 (w), 922 (m), 865 (vs), 858 (vs), 679 cm<sup>-1</sup> (m). Elemental analysis calcd. (%) for C<sub>15</sub>H<sub>29</sub>Cl<sub>4</sub>Cr<sub>2</sub>IO<sub>3.5</sub> (638.09 g mol<sup>-1</sup>): C 28.24, H 4.58; found: C 28.41, H 4.55. Elemental analysis calcd. (%) for no loss of THF: C<sub>17</sub>H<sub>33</sub>Cl<sub>4</sub>Cr<sub>2</sub>IO<sub>4</sub> (674.14 g mol<sup>-1</sup>): C 30.29, H 4.93; <sup>1</sup>H NMR spectroscopy did not show any signals in the range -100 to 100 ppm.

*Characterization of [CrCl<sub>2</sub>I(thf)<sub>3</sub>] (2)*: the microcrystalline powder was washed with toluene and evaporated to dryness (*in vacuo*), giving [CrCl<sub>2</sub>I(thf)<sub>3</sub>] (2). Yield: 0.36 g (120% calculated for a single reaction path producing solely 1 and 2 in equal amounts; thus the high yield indicates an alternative reaction path during the synthesis of 1). DRIFT:  $\nu = 2973$  (w), 2899 (w), 1488 (vw), 1457 (vw), 1448 (vw), 1341 (w), 1295 (vw), 1244 (vw), 1176 (vw), 1140 (vw), 1040 (m), 1011 (s), 958 (vw), 919 (m), 853 (vs), 685 (m), 578 cm<sup>-1</sup> (w). Elemental analysis calcd. (%) for C<sub>12</sub>H<sub>24</sub>Cl<sub>2</sub>CrIO<sub>3</sub> (466.12 g mol<sup>-1</sup>): C 30.92, H 5.18; Found: C 31.16, H 5.00.

*Notes on the synthesis of 1*: **Note A**: when the reaction was repeated at ambient temperature, although a red solution was obtained, only crystals of either [CrCl<sub>3</sub>(thf)<sub>3</sub>] or [CrCl<sub>2</sub>I(thf)<sub>3</sub>] (2) were identified after filtration from insoluble materials. **Note B**: in one synthesis attempt, toluene was added to the THF solution after the initial filtration from 2. This caused formation of additional 2 due to the instability of 1 in toluene. After filtration small crystals of 1 were obtained which also diffracted poorly (contained two molecules within the asymmetric unit, unit cell:  $a = 24.776(8)$  Å,  $b = 11.019(4)$  Å,  $c = 13.817(4)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ). Upon exposure to vacuum a light red powder was obtained and identified by elemental analysis as [Cr<sub>2</sub>Cl<sub>4</sub>(CHI)(thf)<sub>3.25</sub>]. Elemental analysis calcd. (%) for C<sub>14</sub>H<sub>27</sub>Cl<sub>4</sub>Cr<sub>2</sub>IO<sub>3.25</sub> (620.07 g mol<sup>-1</sup>): C 27.11, H 4.38; found C 27.02, H 4.52. **Note C**: when four equivalents of [K(OSi(O*t*Bu)<sub>3</sub>)] were added to a pre-stirred reaction mixture of CrCl<sub>2</sub> (four equiv.)/CHI<sub>3</sub> (one equiv.), the produced [CrCl<sub>2</sub>I(thf)<sub>3</sub>] (2) redissolved. Crystallization from *n*-hexane at -35 °C yielded multiple species, one of which was identified by X-ray crystallography as [Cr<sub>2</sub>Cl<sub>2</sub>(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>(CHI)(thf)<sub>4</sub>] (3), in the form of a few small red block crystals. **Note D**: synthesis of the deuterated derivative [Cr<sub>2</sub>Cl<sub>4</sub>(CHI)(thf)<sub>3.5</sub>] (1<sup>D</sup>) could be achieved by performing the synthesis of 1 with CDI<sub>3</sub> instead of CHI<sub>3</sub>, the resulting product was a red microcrystalline powder. Upon analysis of the product by <sup>2</sup>D NMR spectroscopy using (35.0 mg, 0.06 mmol) only three weak signals in the <sup>2</sup>D NMR were observed for 1<sup>D</sup>. <sup>2</sup>D NMR (76.77 MHz, 300 K, THF(non-deuterated)):  $\delta = 1.69$  (m, THF-d), 2.10 (m), 3.54 ppm (m, THF-d). However, over time only the two peaks remained that were attributed to deuterated THF-d. <sup>2</sup>D NMR (76.77 MHz, 300 K, THF):  $\delta = 1.69$  (m), 3.55 ppm (m); resonances did not change upon heating the reaction mixture at 50 °C for 16 h.

**[Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>I(thf)<sub>3</sub>] (4) from the reaction of [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] with CHI<sub>3</sub> in THF**: [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] (35.3 mg, 0.06 mmol, three equiv), was stirred in THF, and a THF solution of CHI<sub>3</sub> (8.0 mg, 0.02 mmol, one equiv) was added causing an immediate color change to yellowish orange. The solution was stirred for two h, before concentration (under vacuum), and addition of *n*-hexane. Storage at -35 °C gave light yellow, twinned crystals of [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>I(thf)<sub>3</sub>] (4), amongst blue crystals of [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>3</sub>(thf)<sub>2</sub>], identified by unit cell comparisons with the literature.<sup>4</sup> The crystals of 4 were washed with *n*-hexane and dried, yielding ~30 mg (~50%). DRIFT:  $\nu = 2968$  (m), 2927 (w), 1456 (w), 1385 (m), 1362 (s), 1238 (s), 1216 (m), 1196 (s), 1189 (s), 1098 (w), 1087 (m), 1062 (s), 1051 (vs), 1044 (s), 1030 (s), 1001 (s), 942 (s), 922 (w), 908 (s), 895 (w), 871 (vs), 866 (vs), 854 (m), 821 (s), 799 (w), 699 (s), 686 (vs), 641 (w), 626 (vw), 570 (vw), 559 (vw), 537 (w), 521 (w), 506 (m), 480 (s), 480 cm<sup>-1</sup> (vs). Elemental analysis calcd. (%) for C<sub>36</sub>H<sub>78</sub>CrIO<sub>11</sub>Si<sub>2</sub> (922.06 g mol<sup>-1</sup>): C 46.89, H 8.52; found: C45.99, H 7.63.

**[Cr<sub>2</sub>I<sub>2</sub>(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>(CHI<sub>2</sub>)]·<sup>1</sup>/<sub>2</sub>*n*-hexane (5a·<sup>1</sup>/<sub>2</sub>*n*-hexane) from treatment of [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] with one equiv of CHI<sub>3</sub>**: an <sup>1</sup>H NMR tube was charged with [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] (78.0 mg, 0.11 mmol, one equiv) and CHI<sub>3</sub> (53.0 mg, 0.14 mmol, one equiv) was added. Upon dissolution in C<sub>6</sub>D<sub>6</sub> (~0.5 mL) a deep brown solution was obtained. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 300 K):  $\delta = 1.39$  (s, underneath broad peak), 0.03-3.35 (br s), 3.99 ppm (s, CHI<sub>3</sub>). The solution was filtered

and dried (*in vacuo*), *n*-hexane was added and CHI<sub>3</sub> precipitated (~10 mg, recovered: 20%). The supernatant solution was separated from CHI<sub>3</sub>, concentrated, and stored at -35 °C, producing crystals of CHI<sub>3</sub> and purple/yellow dichroic crystals of [Cr<sub>2</sub>I<sub>2</sub>(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>(CHI<sub>2</sub>)]·<sup>1</sup>/<sub>2</sub>*n*-hexane (**5a**·<sup>1</sup>/<sub>2</sub>*n*-hexane). Attempted isolation and purification of **5a** failed, as attempted isolation by fractional crystallization gave only green/brown dichroic block crystals of [Cr<sub>2</sub>I(OSi(O*t*Bu)<sub>3</sub>)<sub>4</sub>]<sup>1</sup>/<sub>2</sub> *n*-hexane (**6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane), indicating that ligand redistribution had occurred.

**[Cr<sub>2</sub>I<sub>2</sub>(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>(CHI<sub>2</sub>)]·<sup>1</sup>/<sub>2</sub>*n*-hexane (**5a**·<sup>1</sup>/<sub>2</sub>*n*-hexane) and [Cr<sub>2</sub>I(OSi(O*t*Bu)<sub>3</sub>)<sub>4</sub>]<sup>1</sup>/<sub>2</sub> *n*-hexane (**6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane) from treatment of [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] with half an equivalent of CHI<sub>3</sub>:** an <sup>1</sup>H NMR tube was charged with [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] (29.0 mg, 0.05 mmol, one equiv) and CHI<sub>3</sub> (10 mg, 0.025 mmol, half an equiv) was added. Upon dissolution in C<sub>6</sub>D<sub>6</sub> (~0.5 mL) a deep brown solution formed. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 300 K): δ = 0.08 (s), 1.38 (s, underneath broadened peak), 1.52 (s, underneath broadened peak), 0.03-3.35 (br s), 3.99 ppm (s, CHI<sub>3</sub>). The reaction mixture was filtered and dried (*in vacuo*), and *n*-hexane was added (2-3 mL), precipitating CHI<sub>3</sub>. The supernatant solution was separated from the precipitate, was concentrated, and stored at -35 °C. Crystals of CHI<sub>3</sub>, [Cr<sub>2</sub>I(OSi(O*t*Bu)<sub>3</sub>)<sub>4</sub>]<sup>1</sup>/<sub>2</sub> *n*-hexane (**6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane), and [Cr<sub>2</sub>I<sub>2</sub>(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>(CHI<sub>2</sub>)]·<sup>1</sup>/<sub>2</sub>*n*-hexane (**5a**·<sup>1</sup>/<sub>2</sub>*n*-hexane) were obtained and identified by unit cell comparisons with the genuine samples. Attempted <sup>2</sup>D NMR spectroscopy of a reaction mixture between [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] (17.7 mg, 0.031 mmol) and CDI<sub>3</sub> (7.8 mg, 0.020 mmol) in toluene led to a spectrum consisting of CDI<sub>3</sub> and deuterated toluene. <sup>2</sup>D NMR (77 MHz, 300 K, THF): δ = 2.11 (s, toluene), 3.93 (s, CDI<sub>3</sub>), 7.09 ppm (m, toluene).

**Cr<sub>2</sub>(OSi(O*t*Bu)<sub>3</sub>)<sub>4</sub>(CHI<sub>2</sub>)]·<sup>1</sup>/<sub>2</sub>*n*-hexane (**5b**·<sup>1</sup>/<sub>2</sub>*n*-hexane) and [Cr<sub>2</sub>I(OSi(O*t*Bu)<sub>3</sub>)<sub>4</sub>]<sup>1</sup>/<sub>2</sub> *n*-hexane (**6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane) from treatment of [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] with a third of an equivalent of CHI<sub>3</sub>:** [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] (91.6 mg, 0.16 mmol, three equiv) and CHI<sub>3</sub> (21.0 mg, 0.05 mmol, one equiv) were combined in toluene (3 mL) with stirring. After one h, the reaction mixture was dried (*in vacuo*), and *n*-hexane was added. Storage at -35 °C, gave dichroic crystals of **6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane, along with orange/red crystals of [Cr<sub>2</sub>(OSi(O*t*Bu)<sub>3</sub>)<sub>4</sub>(CHI<sub>2</sub>)]·<sup>1</sup>/<sub>2</sub>*n*-hexane (**5b**·<sup>1</sup>/<sub>2</sub>*n*-hexane), identified by X-ray crystallography. Attempted separation of **5b** led to continuous contamination of crystalline **6a**. Note: the crystals of **5b**·<sup>1</sup>/<sub>2</sub>*n*-hexane were submerged in crystallography oil, and were noted to rapidly decompose to a yellow amorphous material. Elemental analysis calcd. (%) for **6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane, C<sub>51</sub>H<sub>115</sub>Cr<sub>2</sub>IO<sub>16</sub>Si<sub>4</sub> (1326.70 g mol<sup>-1</sup>, loss of lattice *n*-hexane by pre-drying the crystals prior analysis): C 44.88, H 8.47; found: C 44.48, H 7.71.

**Cr<sub>2</sub>I<sub>2</sub>(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] (**6b**) and [Cr<sub>2</sub>I(OSi(O*t*Bu)<sub>3</sub>)<sub>4</sub>]<sup>1</sup>/<sub>2</sub> *n*-hexane (**6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane) from treatment of [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] with a fourth of an equivalent of CHI<sub>3</sub>:** [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] (94.9 mg, 0.16 mmol, four equiv) and CHI<sub>3</sub> (16.0 mg, 0.04 mmol, one equiv) were combined in toluene (3 mL) with stirring. After one h, the reaction mixture was dried (*in vacuo*), and *n*-hexane was added. Storage at -35 °C, gave crystals of dichroic **6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane, along with colorless crystals of [Cr<sub>2</sub>I<sub>2</sub>(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] (**6b**), identified by X-ray crystallography. Some crystals of **6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane and **6b** were easily separable by hand picking, and both were dried under vacuum prior analysis. Characterization of **6a**: yield: ~14 mg, (~13%); elemental analysis calcd. (%) for **6a**·<sup>1</sup>/<sub>2</sub>*n*-hexane: C<sub>51</sub>H<sub>115</sub>Cr<sub>2</sub>IO<sub>16</sub>Si<sub>4</sub> (1326.70 g mol<sup>-1</sup>, loss of lattice *n*-hexane by pre-drying the crystals prior analysis) C 44.88, H 8.47; found: C 44.74, H 7.94. Characterization **6b**: yield: ~12 mg, (~16%); DRIFT: ν = 2974 (s), 2870 (w), 1471 (m), 1456 (m), 1392 (s), 1367 (vs), 1244 (s), 1191 (m),

1084 (s), 1029 (w), 978 (s), 897 (vs), 819 (m), 800 (w), 707 (s), 620 (m), 541 (vs), 528  $\text{cm}^{-1}$  (vs); elemental analysis calcd. (%) for  $\text{C}_{24}\text{H}_{54}\text{Cr}_2\text{I}_2\text{O}_8\text{Si}_2$  ( $884.66 \text{ g mol}^{-1}$ ): C 32.58, H 6.15; found: 32.09, H 6.06.

## Reactions with TMEDA.

**Reaction between isolated 1/1<sup>D</sup> and TMEDA:** *method a, bulk synthesis:*  $[\text{Cr}_2\text{Cl}_4(\text{CDI})(\text{thf})_{3.5}]$  (34.8 mg, 0.05 mmol, one equiv) was stirred in THF and TMEDA (12.0 mg, 0.01 mmol, two equiv) was added as a THF solution. The mixture was stirred, and after two h, a yellow solution was obtained. Upon storage at  $-35 \text{ }^\circ\text{C}$ , small colorless, poorly diffracting crystals were isolated. However, when the reaction was repeated (at  $-35 \text{ }^\circ\text{C}$ ) and an excess of TMEDA was used (2 drops), a similar color change occurred, and crystals of  $[\text{CrCl}_2(\text{tmeda})_2][\text{I}] \cdot \text{THF}$  ( $7 \cdot \text{THF}$ , containing two molecules within the asymmetric unit) were isolated amongst colorless poorly diffracting crystals. *method b, by <sup>2</sup>D NMR:*  $[\text{Cr}_2\text{Cl}_4(\text{CDI})(\text{thf})_{3.5}]$  (35.0 mg, 0.06 mmol, one equiv) was treated with TMEDA (12.3 mg, 0.01 mmol, two equiv added as a THF solution) in a J. Young NMR tube. The reaction mixture was analysed by <sup>2</sup>D NMR spectroscopy, showing that initially three peaks were present in the <sup>2</sup>D NMR spectrum. <sup>2</sup>D NMR (76.77 MHz, 300 K, THF):  $\delta = 1.69$  (m, THF), 2.16 (m), 3.58 ppm (m, THF). The resonance at 2.15 ppm decreased rapidly (gone within 2 h), until only resonances attributable to deuterated THF-d were observed. <sup>2</sup>D NMR (76.77 MHz, 300 K, THF):  $\delta = 1.70$  (s, THF), 3.57 ppm (s, THF). Heating the reaction did not change the observed resonances.

**$[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{tmeda})]$  (**8**):** addition of excess TMEDA to a *n*-hexane solution of  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2]_2$  caused immediate and quantitative formation of  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{tmeda})]$  (**8**), as brown/colorless block crystals. The crystals were washed with cold *n*-hexane removing excess TMEDA. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , 500 MHz, 300 K):  $\delta = 2.10$  ppm (br s). DRIFT:  $\nu = 2972$  (m), 2900 (w), 2806 (vw), 1716 (vw), 1699 (vw), 1652 (vw), 1558 (vw), 1540 (vw), 1471 (m), 1456 (m), 1383 (m), 1361 (s), 1283 (w), 1237 (s), 1193 (s), 1124 (w), 1085 (m), 1060 (vs), 1049 (vs), 1034 (vs), 1014 (vs), 1007 (vs), 952 (m), 909 (w), 819 (s), 806 (m), 770 (w), 693 (vs), 648 (m), 592  $\text{cm}^{-1}$  (w). Elemental analysis calcd. (%) for  $\text{C}_{30}\text{H}_{72}\text{CrN}_2\text{O}_8\text{Si}_2$  ( $695.02 \text{ g mol}^{-1}$ ): C 51.85, H 10.15, N 4.03; found: C 51.50, H 9.81, N 4.14;  $\mu_{\text{eff}} = 5.73 \text{ B. M}$  ( $0.035 \text{ Mol}$ ,  $\Delta\text{Hz} = 752 \text{ Hz}$ ).

**$[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2\text{I}(\text{tmeda})] \cdot \frac{1}{2}\text{C}_6\text{D}_6$  (**10**· $\frac{1}{2}\text{C}_6\text{D}_6$ ) from the Reaction of **8** with  $\text{CXI}_3$  (X = H or D):** *method a, with CHI<sub>3</sub>:*  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{tmeda})]$  (20.3 mg, 0.03 mmol, two equiv) was dissolved in  $\text{C}_6\text{D}_6$ , and  $\text{CHI}_3$  (5.8 mg, 0.02 mmol, one equiv) was added, generating a dark purple/blue reaction mixture. The reaction mixture was analysed by <sup>1</sup>H NMR spectroscopy where only a large broad resonance was observed. No change was observed in the NMR spectrum when re-analysed after 24 h. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ): 0.10 (s), 0.89 (s), 1.23 (s), 1.38 (s), 2.05 ppm (br s). Attempted isolation of any reactive species led only to the isolation of  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2\text{I}(\text{tmeda})] \cdot \frac{1}{2}\text{C}_6\text{D}_6$  (**10**· $\frac{1}{2}\text{C}_6\text{D}_6$ ), identified as purple and pink crystals. *Method b, with CDI<sub>3</sub>:*  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{tmeda})]$  (25.5 mg, 0.04 mmol, two equiv) was stirred in toluene with  $\text{CDI}_3$  (6.7 mg, 0.02 mmol, one equiv), and then analysed by <sup>2</sup>D NMR spectroscopy. Three peaks were observed which did not change over time. <sup>2</sup>D NMR (76.77 MHz, toluene, 300 K):  $\delta = 2.10$  (m, toluene), 4.10 (m), 7.04 ppm (m, toluene).

## Test and blank reactions.

**CDI<sub>3</sub> exchange with THF:** CDI<sub>3</sub> (30 mg, 0.08 mmol), was dissolved in 0.4 mL THF and was analysed by <sup>2</sup>D NMR spectroscopy, showing only CHI<sub>3</sub>. Over time, two new peaks (next to those of CDI<sub>3</sub>), emerged. <sup>2</sup>D NMR (76.77 MHz, THF, 300 K): δ = 1.68 (s, 0.8 D, THF), 3.54 (s, 1 D, THF), 3.98 ppm (s, 25 D, CDI<sub>3</sub>).

**CDI<sub>3</sub> exchange with toluene:** CDI<sub>3</sub> (30.0 mg, 0.08 mmol) was dissolved in 0.4 mL toluene and analysed by <sup>2</sup>D NMR spectroscopy, showing only CDI<sub>3</sub>. <sup>2</sup>D NMR (76.77 MHz, toluene, 300 K): δ = 2.12 (m, 0.5 D, toluene), 3.96 (s, 31.5 d, CDI<sub>3</sub>), 6.09 (s, 1 D), 7.08 ppm (m, 1 D, toluene).

**One-pot reaction between CrCl<sub>2</sub>, CHI<sub>3</sub>, and benzaldehyde in a 4:1:1 ratio:** CrCl<sub>2</sub> (18.8 mg, 0.15 mmol, four equiv), and benzaldehyde (4.0 mg, 0.04 mmol, 1 equiv added from a standard solution) were stirred in THF-d<sub>8</sub> (1 mL) at -35 °C. Iodoform (15 mg, 0.04 mmol, 1 equiv, dissolved in THF-d<sub>8</sub> (1 mL)) was cooled to -35 °C, and then added dropwise to the above mixture at -35 °C. The reaction mixture was slowly warmed to ambient temperature, leaving a light yellow/orange solution and an orange/red precipitate. The reaction mixture was filtered into a J. Young NMR tube and analysed by <sup>1</sup>H NMR spectroscopy, indicating a mixture of benzaldehyde and (E)-(2-iodovinyl)benzene, in a ratio of approximately 1:1. <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 300 K): δ = 7.00 (d, <sup>3</sup>J<sub>H-H</sub>: 14.8 Hz, 1 H, Ph-CH-C), 7.24 (m, 3 H, Ar-H), 7.30 (m, 2 H, Ar-H), 7.41 (d, <sup>3</sup>J<sub>H-H</sub>: 14.8 Hz, 1 H, C-ClH), 7.49 (m, 2 H, benzaldehyde, 3,5-Ar-H), 7.56 (m, 1 H, benzaldehyde, 4-Ar-H), 7.82 (m, 2 H, benzaldehyde, 2,6-Ar-H), 9.91 ppm (s, 1 H, benzaldehyde, CHO); note: potential resonances for the (Z)-(2-iodovinyl)benzene isomer could not be observed due to the overlapping resonances of the aldehyde.

**Treatment of Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub> with benzaldehyde:** [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] (18.7 mg, 0.03 mmol, one equiv) was dissolved in C<sub>6</sub>D<sub>6</sub>, and benzaldehyde (1.7 mg, 0.02 mmol, half an equiv) was added as a C<sub>6</sub>D<sub>6</sub> solution. The solution turned immediately light green upon addition. <sup>1</sup>H NMR spectroscopy indicated the appearance of only paramagnetically broadened signals.

## Reactions of the organochromium reagents with either benzaldehyde or 4-*tert*-butyl-cyclohexanone.

**Reaction between isolated **1** and half an equiv of benzaldehyde:** **1** (27.6 mg, 0.04 mmol, one equiv) was dissolved in THF-d<sub>8</sub> and cooled to -35 °C. Benzaldehyde (2.2 mg, 0.03 mmol, half an equiv as a cold THF-d<sub>8</sub> solution), was added dropwise to the stirring solution of **1** at -35 °C. The reaction mixture was warmed to ambient temperature over the space of 10 min and then filtered into a J. Young NMR tube. <sup>1</sup>H NMR spectroscopic analysis indicated the formation of both (E)-(2-iodovinyl)benzene (94%) and (Z)-(2-iodovinyl)benzene (6%) in a ratio of 15.7:1.0.

**Reaction between isolated **1** and one equiv of benzaldehyde:** **1** (10.3 mg, 0.016 mmol, one equiv in slight excess) was dissolved in THF-d<sub>8</sub> and cooled to -35 °C. Benzaldehyde (1.5 mg, 0.014 mmol, one equiv as a cold THF-d<sub>8</sub> solution), was added dropwise to the stirring solution of **1** at -35 °C. The reaction mixture was warmed to ambient temperature

over the space of 10 min and then filtered into a J. Young NMR tube.  $^1\text{H}$  NMR analysis indicated the formation of both (*E*)-(2-iodovinyl)benzene (94%) and (*Z*)-(2-iodovinyl)benzene (6%). No resonances for benzaldehyde were observed.

**Treatment of *in situ* generated 5a and benzaldehyde:**  $[\text{Cr}(\text{OSi}(\text{OtBu})_3)_2]$  (10.3 mg, 0.02 mmol, four equiv) and  $\text{CHI}_3$  (3.5 mg, 0.01 mmol, two equiv) were stirred in  $\text{C}_6\text{D}_6$ , giving a green/brown solution. Benzaldehyde (0.5 mg, 0.05 mmol, one equiv) was added as a  $\text{C}_6\text{D}_6$  solution, causing a color change to light brown.  $^1\text{H}$  NMR spectroscopy indicated the formation of (*E/Z*)-(2-iodovinyl)benzene.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , large broadened paramagnetic resonances below 5.00 ppm are not presented, some aromatic resonances of (*E/Z*)-(2-iodovinyl)benzene located under the  $\text{C}_6\text{D}_6$  resonances): 6.12 (d,  $^3J_{\text{H-H}}$ : 8.40 Hz, 1 H, CHI, resonance disappeared when the reaction was repeated with  $\text{CDI}_3$ ), 6.41 (d,  $^3J_{\text{H-H}}$ : 14.86 Hz,  $\sim 0.5$  H, resonance disappeared when the reaction was repeated with  $\text{CDI}_3$ ), 6.82 (m, 2 H, Ar-3,5 H), 6.98 (m,  $\sim 2$  H, located near  $\text{C}_6\text{D}_6$  satellite, Ar-H(4) + Ar-CH=C), 7.50 ppm (*d* of multiplets,  $^3J_{\text{H-H}}$ : 7.51 Hz, 2 H, Ar-H(3,6)).

**Reaction between *in situ* generated  $[\text{Cr}(\text{OSi}(\text{OtBu})_3)_2(\text{tmeda-CHI})][\text{I}]$  (9) with benzaldehyde:**  $[\text{Cr}(\text{OSi}(\text{OtBu})_3)_2(\text{tmeda})]$  (8, 22.0 mg, 0.03 mmol, two equiv) was dissolved in  $\text{C}_6\text{D}_6$ , and  $\text{CHI}_3$  (6.3 mg, 0.02 mmol, one equiv in slight excess) was added. To the formed dark purple solution, benzaldehyde (1.5 mg, 0.01 mmol, as a  $\text{C}_6\text{D}_6$  solution), was added causing an immediate color change to lime green.  $^1\text{H}$  NMR spectroscopic analysis did not indicate the formation of any (*Z*)-(2-iodovinyl)benzene, and only broadened resonances (see Figure S11). Crystallization from *n*-hexane/ $\text{C}_6\text{D}_6$  led to poor quality lime green crystals of  $[\text{Cr}(\text{OSi}(\text{OtBu})_3)_2(\text{I}(\text{tmeda})(\text{benzaldehyde}))]\cdot\text{C}_6\text{D}_6$  (11· $\text{C}_6\text{D}_6$ ).

**Reaction between isolated 1 and 4-*tert*-butyl-cyclohexanone:** 1 (7.0 mg, 0.01 mmol, one equiv in slight excess) was dissolved in THF- $\text{d}_8$ , and cooled to  $-35$  °C. 4-*tert*-Butyl-cyclohexanone (1.5 mg, 0.01 mmol, one equiv) was added, as a cold THF- $\text{d}_8$  solution, dropwise to the stirring solution of 1 at  $-35$  °C. The reaction mixture was warmed to ambient temperature over 10 min giving a red/orange solution. Initial  $^1\text{H}$  NMR spectroscopic analysis indicated the formation of 1-(*tert*-butyl)-4-(iodomethylene)cyclohexane (69%) together with unreacted 4-*tert*-butyl-cyclohexanone (29%), in a ratio of approximately 2.3:1. The NMR tube was first warmed in a water bath (approx. 40 °C) for 20 min, before it was heated at 50 °C for ten min within the spectrometer. Analysis at ambient temperature gave a new ratio of 5.3:1, or 84% conversion of 4-*tert*-butyl-cyclohexanone.

**Treatment of *in situ* generated 5a with 4-*tert*-butylcyclohexanone:**  $[\text{Cr}(\text{OSi}(\text{OtBu})_3)_2]$  (12.4 mg, 0.021 mmol, four equiv) and  $\text{CHI}_3$  (4.0 mg, 0.01 mmol, two equiv) were stirred in  $\text{C}_6\text{D}_6$ . 4-*tert*-Butylcyclohexanone (1 mg, 0.01 mmol, one equiv) was added.  $^1\text{H}$  NMR spectroscopy indicated no reaction. Re-analysis by  $^1\text{H}$  NMR spectroscopy after 16 h indicated the formation of minor resonances which could be attributable to 1-(*tert*-butyl)-4-(iodomethylene)cyclohexane in minute amounts. The reaction mixture was heated to 50 °C for 24 h, but only decomposition was observed.

**Isolation of crystalline  $[\text{Cr}(\text{OSi}(\text{OtBu})_3)_2(\text{tmeda-CHI})][\text{I}]\cdot\text{C}_6\text{D}_6$  (9· $\text{C}_6\text{D}_6$ ) from the reaction of  $[\text{Cr}(\text{OSi}(\text{OtBu})_3)_2(\text{tmeda})]$  (10) with  $\text{CHI}_3$  and 4-*tert*-butylcyclohexanone:**  $[\text{Cr}(\text{OSi}(\text{OtBu})_3)_2(\text{tmeda})]$  (10, 10.0 mg, 0.01 mmol, two equiv) was dissolved in  $\text{C}_6\text{D}_6$  and  $\text{CHI}_3$  (3.0 mg, 0.01 mmol, one equiv in slight excess) was added. To the resulting dark purple solution 4-*tert*-butyl-cyclohexanone (1.0 mg, 0.01 mmol, one equiv, as a  $\text{C}_6\text{D}_6$  solution) was

added, and the solution lightened in color.  $^1\text{H}$  NMR spectroscopic analysis indicated minimal to no formation of 1-(*tert*-butyl)-4-(iodomethylene)cyclohexane. After several h, small blue/purple dichroic crystals of  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{tmeda}-\text{CHI})][\text{I}]\cdot\text{C}_6\text{D}_6$  (**9**· $\text{C}_6\text{D}_6$ ) had formed, along with crystals of  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2\text{I}(\text{tmeda})]\cdot\text{C}_6\text{D}_6$  (**10**), and colorless poorly diffracting crystals. Re-analysis by  $^1\text{H}$  NMR spectroscopy indicated an apparent decomposition process by the appearance of multiple new peaks in the spectrum.

#### **Preliminary reactions between organochromium reagents and allyl benzyl ether.**

**Reaction between isolated  $1^{\text{D}}$  and an equiv of allyl benzyl ether, with addition of TMEDA:**  $1^{\text{D}}$  (18.8 mg, 0.03 mmol, one equiv) was stirred in THF, and TMEDA (7.0 mg, 0.06 mmol, two equiv) was added as a THF solution, followed by the immediate addition of allyl benzyl ether (4.3 mg, 0.03 mmol, added as a THF solution). The reaction mixture was stirred for two h giving a light yellow solution. The reaction mixture was stored at  $-35\text{ }^\circ\text{C}$  for several h to remove insoluble crystalline material (crystals diffracted poorly and no solid-state structure could be resolved). The reaction mixture was filtered into a J. Young NMR Tube, and  $^2\text{D}$  NMR spectroscopy indicated the *cis-trans* mixture of (2-iodocyclopropyl)methyl benzyl ether.  $^2\text{D}$  NMR (76.77 MHz, 300 K, THF):  $\delta = 1.69$  (s, THF), 2.14 (s, 3.25 D, *trans*), 2.25 (m, 1 D, *cis*), 3.54 ppm (s, THF).

**Reaction between in situ generated  $5a^{\text{D}}$  and allyl benzyl ether:**  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2]$  (4.7 mg, 0.08 mmol, four equiv) and  $\text{CDI}_3$  (16 mg, 0.04 mmol, two equiv) were stirred in toluene giving a green/light brown solution. Allyl benzyl ether (3.0 mg, 0.02 mmol, one equiv) was added as a toluene solution. After stirring for several minutes, the reaction mixture turned brown. The contents were transferred into a J. Young NMR tube and analysed by  $^2\text{D}$  NMR spectroscopy, which did not indicate the formation of any (2-iodocyclopropyl)methyl benzyl ether, and only resonances for  $\text{CDI}_3$  and toluene were observed.  $^2\text{D}$  NMR (76.77 MHz, toluene, 300 K):  $\delta = 2.11$  (m, toluene), 3.95 (m,  $\text{CDI}_3$ ), 7.09 ppm (toluene).

**Reaction between in situ generated  $9^{\text{D}}$  and allyl benzyl ether:** **8** (24.0 mg, 0.03 mmol, two equiv) was dissolved in toluene and  $\text{CDI}_3$  (6.7 mg, 0.02 mmol, one equiv) was added. The reaction mixture turned dark purple, and allyl benzyl ether (2.5 mg, 0.02 mmol, one equiv) was added. After stirring for several h at ambient temperature, filtration from formed insoluble species, and analysis by  $^2\text{D}$  NMR spectroscopy indicated no formation of (2-iodocyclopropyl)methyl benzyl ether, giving a spectrum containing only  $\text{CDI}_3$  and toluene.

## X-ray crystallography

All compounds were examined on a 'Bruker APEX-II CCD' diffractometer. The crystals were mounted on a fiber loop in paratone-*n* crystallography oil. Absorption corrections were completed using Apex II program suite.<sup>5</sup> Structural solutions were obtained by either charge flipping or direct methods and refined using full matrix least squares methods against  $F^2$  using SHELX2013,<sup>6,7</sup> within the OLEX 2 graphical interface.<sup>8</sup> A list of the parameters are found in Table S1.

**Table S1.** X-ray crystallographic parameters for complexes **2-6a**

Compound	[CrCl <sub>2</sub> (thf) <sub>3</sub> ]	[Cr <sub>2</sub> Cl <sub>2</sub> (OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>2</sub> (CHI)(thf) <sub>4</sub> ]	[Cr <sub>2</sub> (OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>2</sub> I(thf) <sub>3</sub> ]	[Cr <sub>2</sub> I <sub>2</sub> (OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>2</sub> (CHI <sub>2</sub> ) <sub>2</sub> · <sup>1/2</sup> <i>n</i> -hexane	[Cr <sub>2</sub> (OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>4</sub> (CHI <sub>2</sub> ) <sub>2</sub> · <sup>1/2</sup> <i>n</i> -hexane	[Cr <sub>2</sub> I(OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>4</sub> · <sup>1/2</sup> <i>n</i> -hexane
Sample code	<b>2</b>	<b>3</b>	<b>4</b>	<b>5a</b> · <sup>1/2</sup> <i>n</i> -hexane	<b>5b</b> · <sup>1/2</sup> <i>n</i> -hexane	<b>6a</b> · <sup>1/2</sup> <i>n</i> -hexane
CCDC No.#	1811553	1811554	1858040	1811552	1811547	1811556
Empirical formula	C <sub>12</sub> H <sub>24</sub> Cl <sub>2</sub> CrIO <sub>3</sub>	C <sub>41</sub> H <sub>87</sub> Cl <sub>2</sub> Cr <sub>2</sub> IO <sub>12</sub> Si <sub>2</sub>	C <sub>36</sub> H <sub>78</sub> CrIO <sub>11</sub> Si <sub>2</sub>	C <sub>28</sub> H <sub>62</sub> Cr <sub>2</sub> I <sub>4</sub> O <sub>8</sub> Si <sub>2</sub>	C <sub>52</sub> H <sub>116</sub> Cr <sub>2</sub> I <sub>2</sub> O <sub>16</sub> Si <sub>4</sub>	C <sub>49.5</sub> H <sub>111.5</sub> Cr <sub>2</sub> IO <sub>16</sub> Si <sub>4</sub>
Formula weight	466.12	1130.09	922.06	1194.56	1467.61	1306.15
Temperature/K	100	100	99.99	100	100	100.1
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a/Å	8.3985(2)	16.4739(12)	10.4074(9)	10.0937(14)	13.6739(4)	13.3190(8)
b/Å	12.6561(4)	17.6022(12)	15.2740(14)	11.5433(16)	14.7859(4)	13.6739(8)
c/Å	15.8544(4)	20.0801(14)	17.3686(17)	21.451(3)	19.0519(5)	21.8226(13)
α/°	90.00	90.00	114.788(5)	79.581(3)	94.5434(14)	80.7633(9)
β/°	92.0756(13)	109.3055(11)	90.356(5)	89.987(3)	107.6252(14)	80.5611(9)
γ/°	90.00	90.00	109.864(5)	66.108(3)	93.1097(14)	62.7355(9)
Volume/Å <sup>3</sup>	1684.09(8)	5495.3(7)	2321.4(4)	2240.1(5)	3647.15(17)	3468.4(4)
Z	4	4	2	2	2	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.838	1.366	1.319	1.771	1.336	1.251
μ/mm <sup>-1</sup>	2.830	1.149	1.012	3.332	1.264	0.882
F(000)	924.0	2368.0	974	1164.0	1532.0	1387.0
Crystal size/mm <sup>3</sup>	0.1 × 0.1 × 0.05	0.2 × 0.2 × 0.1	0.3 × 0.2 × 0.05	0.2 × 0.1 × 0.1	0.4 × 0.4 × 0.3	0.3 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.12 to 55	2.78 to 60.16	2.62 to 50.14	3.88 to 52	3.24 to 56.74	1.9 to 54.38
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20	-23 ≤ h ≤ 23, -24 ≤ k ≤ 24, -28 ≤ l ≤ 28	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -17 ≤ l ≤ 20	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -26 ≤ l ≤ 26	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -25 ≤ l ≤ 25	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -28 ≤ l ≤ 28
Reflections collected	29060	121258	7730	36768	117347	49689
Independent reflections	3874 [R <sub>int</sub> = 0.0271, R <sub>sigma</sub> = 0.0168]	16111 [R <sub>int</sub> = 0.0765, R <sub>sigma</sub> = 0.0462]	7730 [R <sub>int</sub> = 0.0000, R <sub>sigma</sub> = 0.0758]	8677 [R <sub>int</sub> = 0.0453, R <sub>sigma</sub> = 0.0407]	18203 [R <sub>int</sub> = 0.0312, R <sub>sigma</sub> = 0.0220]	15420 [R <sub>int</sub> = 0.0434, R <sub>sigma</sub> = 0.0435]
Data/restraints/parameters	3874/0/172	16111/0/612	7730/78/479	8677/0/425	18203/0/722	15420/18/714
Goodness-of-fit on F <sup>2</sup> [a]	1.070	1.098	1.247	1.069	1.050	1.132
Final R indexes [I ≥ 2σ(I)] <sup>[b]</sup> [c]	R <sub>1</sub> = 0.0312, wR <sub>2</sub> = 0.0896	R <sub>1</sub> = 0.0439, wR <sub>2</sub> = 0.0985	R <sub>1</sub> = 0.0977, wR <sub>2</sub> = 0.2493	R <sub>1</sub> = 0.0654, wR <sub>2</sub> = 0.1821	R <sub>1</sub> = 0.0287, wR <sub>2</sub> = 0.0641	R <sub>1</sub> = 0.0339, wR <sub>2</sub> = 0.0964
Final R indexes [all data]	R <sub>1</sub> = 0.0361, wR <sub>2</sub> = 0.0926	R <sub>1</sub> = 0.0726, wR <sub>2</sub> = 0.1152	R <sub>1</sub> = 0.1163, wR <sub>2</sub> = 0.2593	R <sub>1</sub> = 0.0784, wR <sub>2</sub> = 0.1940	R <sub>1</sub> = 0.0396, wR <sub>2</sub> = 0.0704	R <sub>1</sub> = 0.0453, wR <sub>2</sub> = 0.1144
Largest diff. peak/hole / e Å <sup>-3</sup>	2.09/-1.07	1.52/-1.17	2.40/-1.96	3.71/-2.16	2.01/-0.87	2.02/-0.74

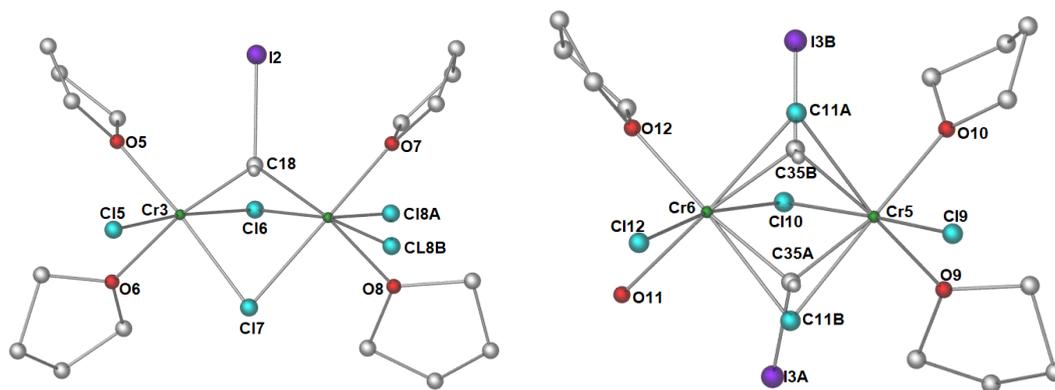
<sup>[a]</sup>GOF = [Σw(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>) / (n<sub>o</sub> - n<sub>p</sub>)]<sup>1/2</sup>. <sup>[b]</sup>R<sub>1</sub> = Σ(|F<sub>o</sub> - |F<sub>c</sub>||) / Σ|F<sub>o</sub>|, F<sub>o</sub> > 4σ(F<sub>o</sub>). <sup>[c]</sup>wR<sub>2</sub> = {Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>) / Σ[w(F<sub>o</sub><sup>2</sup>)]}<sup>1/2</sup>.

**Table S1 continued. X-ray crystallographic parameters for complexes 6b-10**

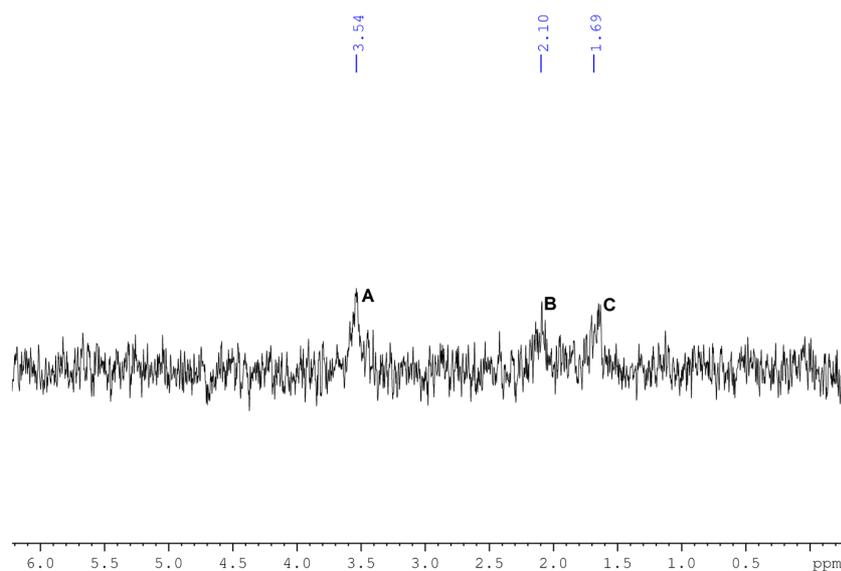
Compound	[Cr <sub>2</sub> I <sub>2</sub> (OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>2</sub> ]	[CrCl <sub>2</sub> (tmeda)]I·thf	[Cr(OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>2</sub> (tmeda)]	[Cr(OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>2</sub> (CHIN(Me) <sub>2</sub> C <sub>2</sub> H <sub>4</sub> NMe <sub>2</sub> )](I). C <sub>6</sub> D <sub>6</sub>	[Cr(OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>2</sub> (tmeda)]·1/2C <sub>6</sub> D <sub>6</sub>
<b>Sample code</b>	<b>6b</b>	<b>7·THF</b>	<b>8</b>	<b>9·C<sub>6</sub>D<sub>6</sub></b>	<b>10·1/2C<sub>6</sub>D<sub>6</sub></b>
<b>CCDC No.#</b>	1811548	1811550	1811555	1811551	1811549
<b>Empirical formula</b>	C <sub>24</sub> H <sub>54</sub> Cr <sub>2</sub> I <sub>2</sub> O <sub>8</sub> Si <sub>2</sub>	C <sub>16</sub> H <sub>40</sub> Cl <sub>2</sub> CrIN <sub>4</sub> O	C <sub>30</sub> H <sub>70</sub> CrN <sub>2</sub> O <sub>8</sub> Si <sub>2</sub>	C <sub>43.75</sub> H <sub>77</sub> CrI <sub>2</sub> N <sub>2</sub> O <sub>8</sub> Si <sub>2</sub>	C <sub>33</sub> H <sub>73</sub> CrIN <sub>2</sub> O <sub>8</sub> Si <sub>2</sub>
<b>Formula weight</b>	884.65	554.32	695.06	1121.05	861.01
<b>Temperature/K</b>	100	100	100	150.0	150.0
<b>Crystal system</b>	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
<b>Space group</b>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<b>a/Å</b>	17.8832(19)	11.379(2)	10.4960(9)	27.7924(18)	9.2746(13)
<b>b/Å</b>	9.1254(10)	11.659(2)	17.3331(14)	9.4487(6)	14.813(2)
<b>c/Å</b>	23.860(3)	18.521(4)	10.9890(9)	42.685(3)	17.529(2)
<b>α/°</b>	90.00	90.00	90.00	90.00	82.759(2)
<b>β/°</b>	104.6588(19)	102.867(4)	96.7186(12)	101.3700(10)	87.291(2)
<b>γ/°</b>	90.00	90.00	90.00	90.00	73.148(2)
<b>Volume/Å<sup>3</sup></b>	3767.0(7)	2395.5(8)	1985.5(3)	10989.2(12)	2286.3(5)
<b>Z</b>	4	4	2	8	2
<b>ρ<sub>calc</sub>/cm<sup>3</sup></b>	1.560	1.537	1.163	1.355	1.251
<b>μ/mm<sup>-1</sup></b>	2.316	2.001	0.392	1.420	1.020
<b>F(000)</b>	1776.0	1132.0	760.0	4604.0	908.0
<b>Crystal size/mm<sup>3</sup></b>	0.1 × 0.05 × 0.05	0.1 × 0.01 × 0.01	0.47 × 0.414 × 0.255	0.5 × 0.2 × 0.2	0.4 × 0.2 × 0.2
<b>Radiation</b>	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
<b>2θ range for data collection/°</b>	2.56 to 53.6	3.5 to 52.3	3.74 to 60.12	2.98 to 61.98	2.9 to 57.34
<b>Index ranges</b>	-22 ≤ h ≤ 22, -11 ≤ k ≤ 11, -30 ≤ l ≤ 28	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -22 ≤ l ≤ 22	-14 ≤ h ≤ 14, -24 ≤ k ≤ 24, -15 ≤ l ≤ 15	-39 ≤ h ≤ 40, -13 ≤ k ≤ 13, -61 ≤ l ≤ 61	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23
<b>Reflections collected</b>	46122	20541	26916	149998	71129
<b>Independent reflections</b>	8049 [R <sub>int</sub> = 0.0897, R <sub>sigma</sub> = 0.0556]	4769 [R <sub>int</sub> = 0.1572, R <sub>sigma</sub> = 0.1732]	11617 [R <sub>int</sub> = 0.0444, R <sub>sigma</sub> = 0.0668]	17429 [R <sub>int</sub> = 0.0421, R <sub>sigma</sub> = 0.0237]	11751 [R <sub>int</sub> = 0.0800, R <sub>sigma</sub> = 0.0529]
<b>Data/restraints/parameters</b>	8049/24/381	4769/36/236	11617/1/410	17429/68/611	11751/0/446
<b>Goodness-of-fit on F<sup>2</sup>[a]</b>	1.054	1.131	1.016	1.194	1.044
<b>Final R indexes [I ≥ 2σ(I)]<sup>[b]</sup>[c]</b>	R <sub>1</sub> = 0.0398, wR <sub>2</sub> = 0.0793	R <sub>1</sub> = 0.1002, wR <sub>2</sub> = 0.1315	R <sub>1</sub> = 0.0382, wR <sub>2</sub> = 0.0766	R <sub>1</sub> = 0.0456, wR <sub>2</sub> = 0.1116	R <sub>1</sub> = 0.0309, wR <sub>2</sub> = 0.0680
<b>Final R indexes [all data]</b>	R <sub>1</sub> = 0.0661, wR <sub>2</sub> = 0.0880	R <sub>1</sub> = 0.1768, wR <sub>2</sub> = 0.1500	R <sub>1</sub> = 0.0462, wR <sub>2</sub> = 0.0810	R <sub>1</sub> = 0.0567, wR <sub>2</sub> = 0.1216	R <sub>1</sub> = 0.0537, wR <sub>2</sub> = 0.0806
<b>Largest diff. peak/hole / e Å<sup>-3</sup></b>	1.31/-0.87	2.36/-1.77	0.35/-0.35	1.58/-1.04	0.50/-0.60

<sup>[a]</sup>GOF =  $[\sum w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$ . <sup>[b]</sup>R<sub>1</sub> =  $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ , F<sub>0</sub> > 4σ(F<sub>0</sub>). <sup>[c]</sup>wR<sub>2</sub> =  $\{\Sigma[w(F_o^2 - F_c^2)^2 / \Sigma[w(F_o^2)^2]]\}^{1/2}$ .

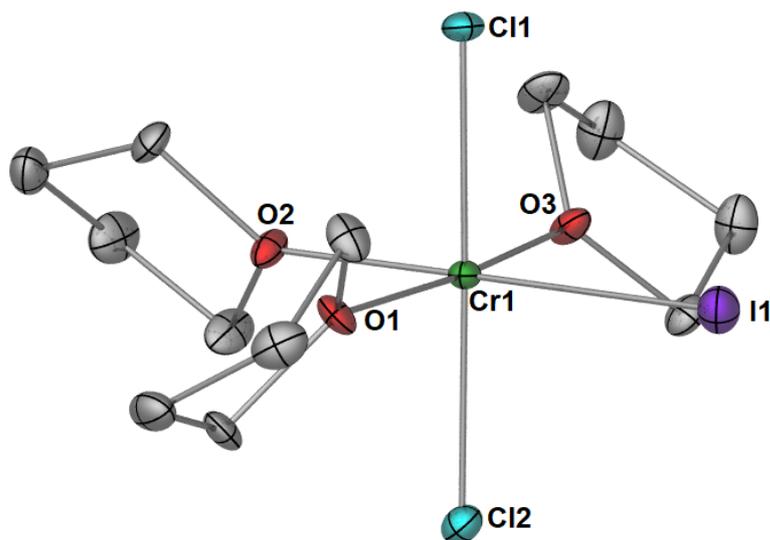
## Supplementary Figures and Schemes Associated with the Manuscript (Figures S1-S14)



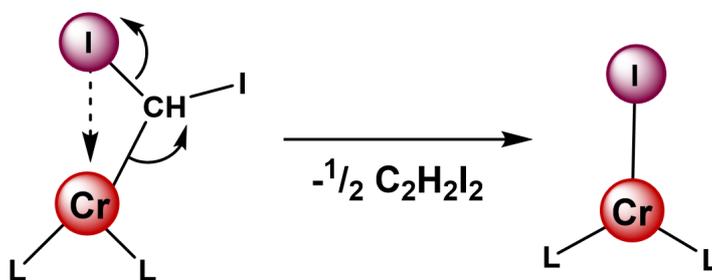
**Figure S1.** Connectivity structure of  $[\text{Cr}_2\text{Cl}_4(\text{CHI})(\text{thf})_4]$  (**1**), showing two of the three molecules (Cr3 & Cr4, Cr5 & Cr6) of the asymmetric unit (see Figure 1 for Cr1 & Cr2). Complex **1** crystallized as slightly-twinned red prisms. Although the raw crystal data appeared acceptable (data at resolution inf. – 0.83: % completeness = 99.8, redundancy = 10.44, mean intensity = 5.6, mean intensity/ $\sigma$  = 14.78,  $R(\text{int}) = 0.0974$ ,  $R\sigma = 0.0525$ ), no suitable structural solution beyond connectivity was obtained. A range of space groups was attempted (e.g.,  $Pmmm$ ,  $P2(1)2(1)2(1)$ ,  $Pmm2$ ,  $P222$ ), but only  $P2(1)2(1)2$  gave connectivity. Poor quality crystal data, together with ligand disorder (e.g. Cl8, C35, I3, C11) also caused difficulty in determining an adequate structural solution, for instance the carbon atoms of O11 (thf) could not be refined and Cl/CHI disorder was apparent across all three molecules of the asymmetric unit. In addition, the terminal chlorido ligands Cl2 (Figure 1), Cl8, and Cl12 were either highly disordered over several positions or hold a partial iodido character, e.g.,  $[\text{Cr}_2\text{Cl}_{3.75}\text{I}_{0.25}(\text{CHI})(\text{thf})_4]$ , but due to the poor crystal quality this could not be definitively determined. The obtained unit cell was:  $a = 17.269(2) \text{ \AA}$ ,  $b = 41.044(4) \text{ \AA}$ ,  $c = 10.940(1) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ .



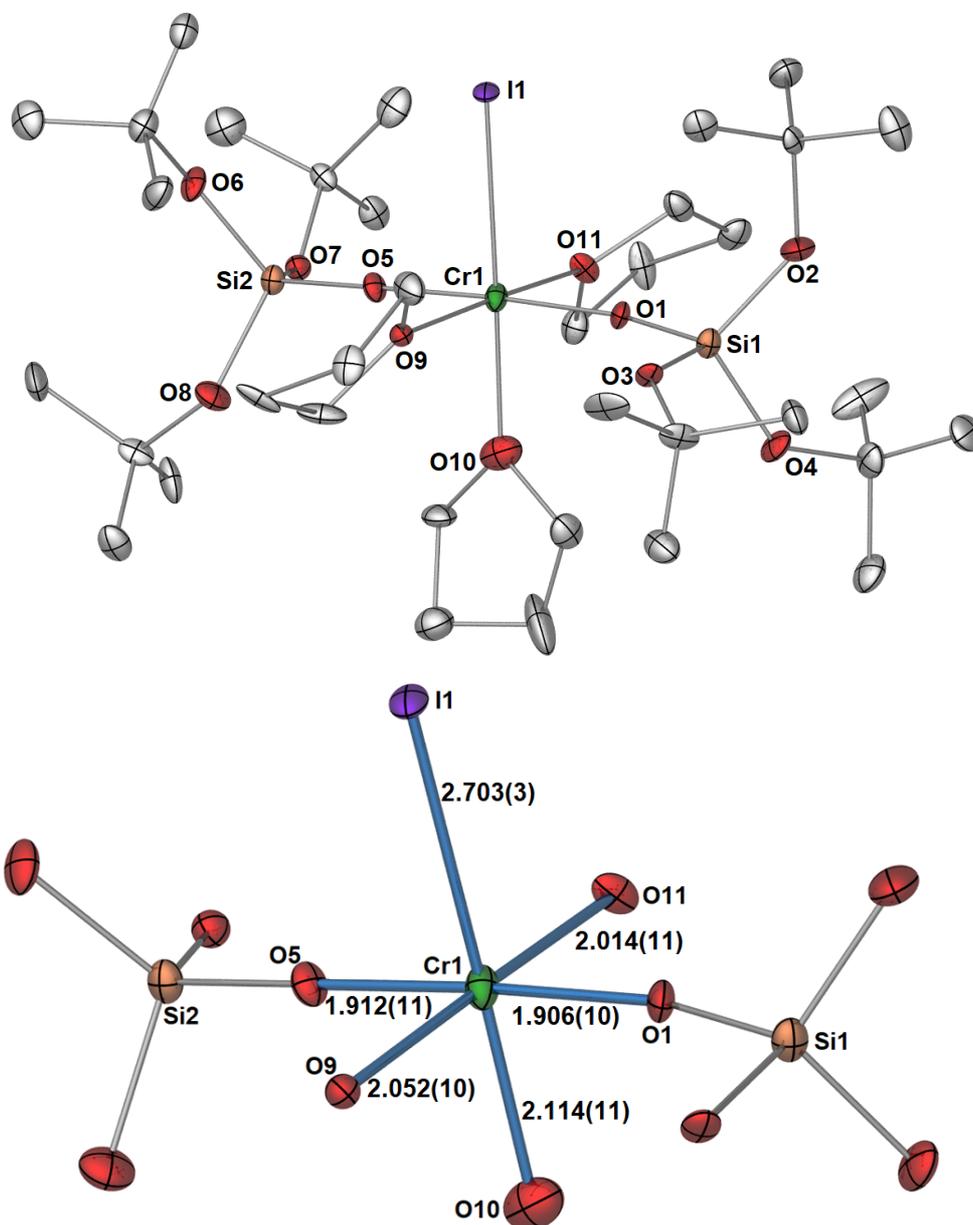
**Figure S2.**  $^2\text{D}$  NMR spectrum (76.77 MHz, THF, 300 K) of  $[\text{Cr}_2\text{Cl}_4(\text{CDI})(\text{thf})_{3.5}]$  (**1<sup>P</sup>**). The small resonance at 2.10 ppm (**B**) disappeared, and the resonances for THF-d (**A** and **C**) increased over time. After 5 h at ambient temperature, only resonances **A** and **C** remained.



**Figure S3.** Crystal structure of  $[\text{CrCl}_2\text{I}(\text{thf})_3]$  (**2**) with atomic displacement ellipsoids set at 50% probability. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **2**: Cr1-Cl1: 2.3135(9), Cr1-Cl2: 2.3312(10), Cr1-I1: 2.6887(6), Cr1-O1: 2.014(3), Cr1-O2: 2.068(2), Cr1-O3: 2.023(3), Cl1-Cr1-Cl2: 179.00(4), Cl1-Cr1-I1: 89.83(3), Cl2-Cr1-I1: 90.90(3), Cl1-Cr1-O1: 88.89(8), Cl1-Cr1-O2: 90.34(7), Cl1-Cr1-O3: 89.77(7), I1-Cr1-O1: 92.68(7), I1-Cr1-O2: 179.57(8), I1-Cr1-O3: 93.90(7).

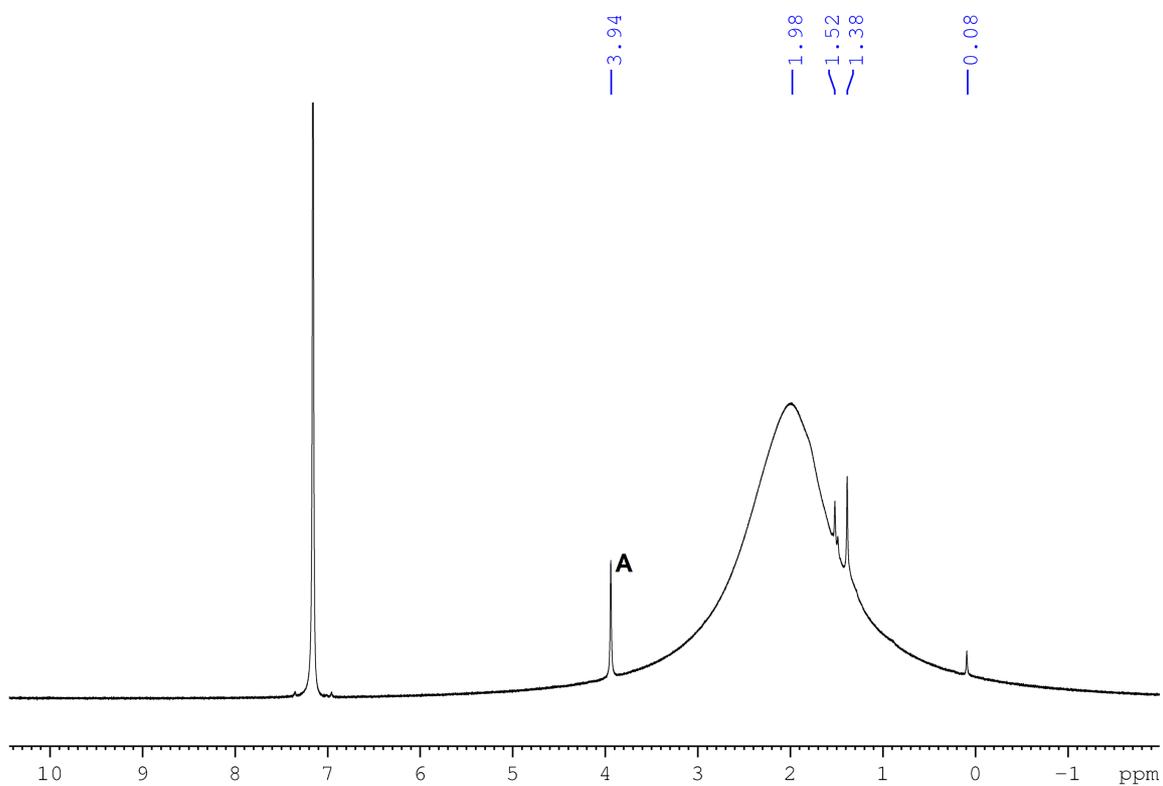


**Scheme S1.** Likely formation of a Cr-I species through decomposition of a Cr-CHI<sub>2</sub> intermediate.

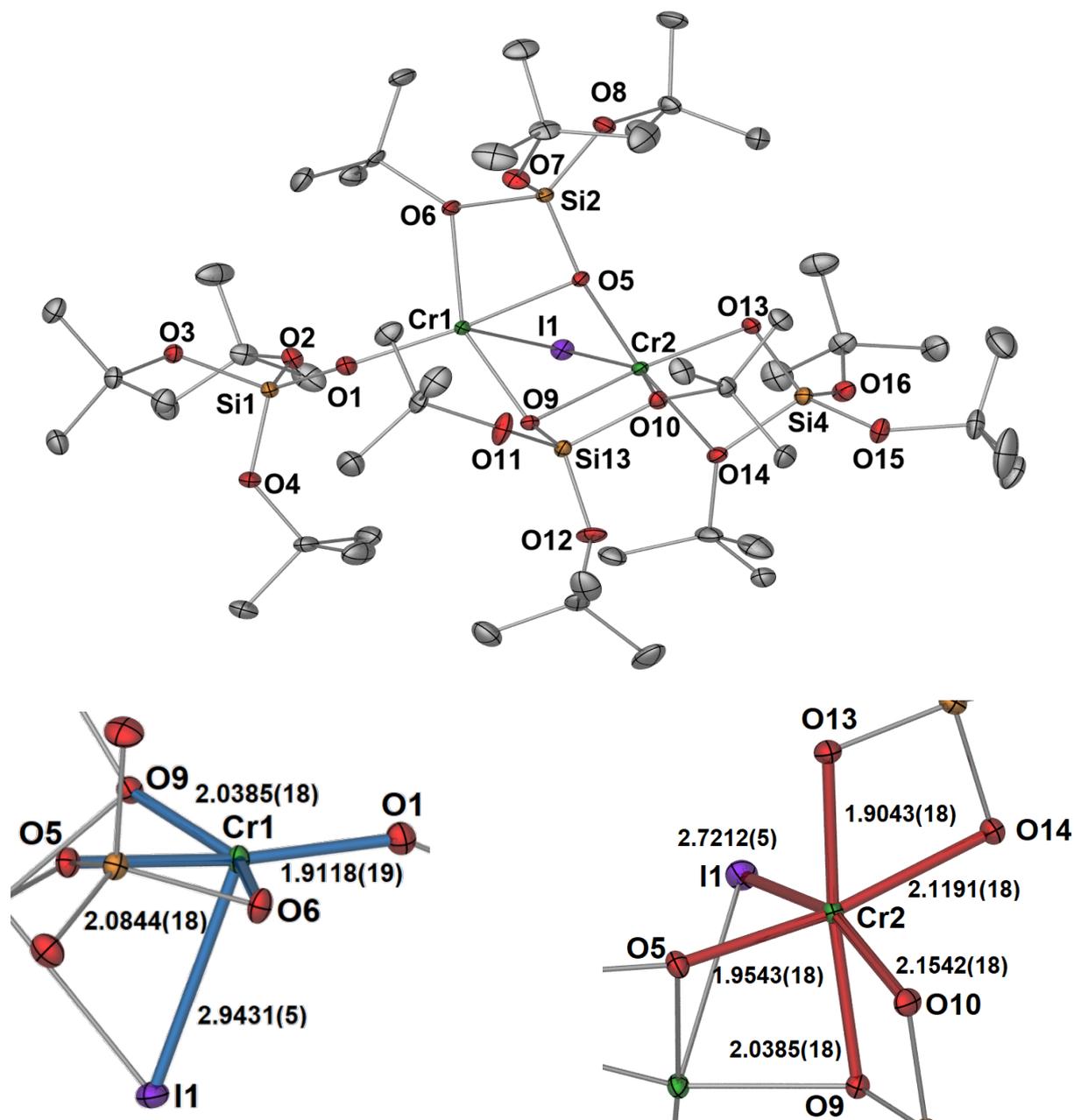


**Figure S4.** Structure of  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2\text{I}(\text{thf})_3]$  (**4**) along with selected bond lengths ( $\text{\AA}$ ). Atomic displacement ellipsoids set at 35% probability. Hydrogen atoms omitted for clarity. Selected bond angles for **4**:

atom	atom	atom	angle ( $^\circ$ )	atom	atom	atom	angle ( $^\circ$ )	atom	atom	atom	angle ( $^\circ$ )
O11	Cr1	I1	93.8(3)	O10	Cr1	I1	178.3(3)	O1	Cr1	O5	177.3(4)
O11	Cr1	O9	175.7(4)	O1	Cr1	I1	90.0(3)	O5	Cr1	I1	92.6(3)
O11	Cr1	O10	86.7(4)	O1	Cr1	O11	88.9(4)	O5	Cr1	O11	91.2(5)
O9	Cr1	I1	90.5(3)	O1	Cr1	O9	90.7(4)	O5	Cr1	O9	89.0(4)
O9	Cr1	O10	89.0(4)	O1	Cr1	O10	88.4(4)	O5	Cr1	O10	89.0(4)

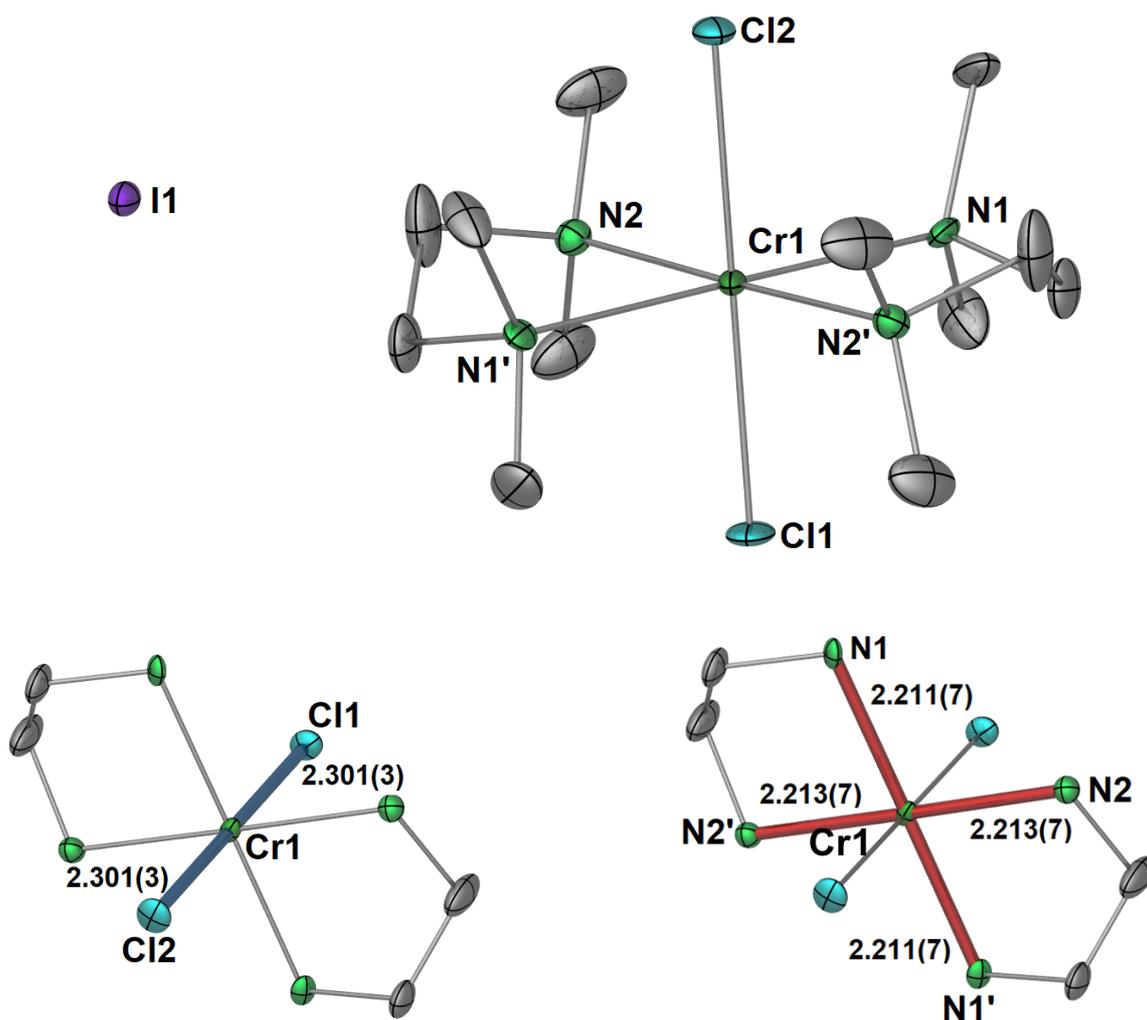


**Figure S5.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ , 300 K) of the reaction between  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2]$  and half an equiv of  $\text{CHI}_3$ . Spectrum indicates a large amount of unreacted  $\text{CHI}_3$  (A) within the reaction mixture.



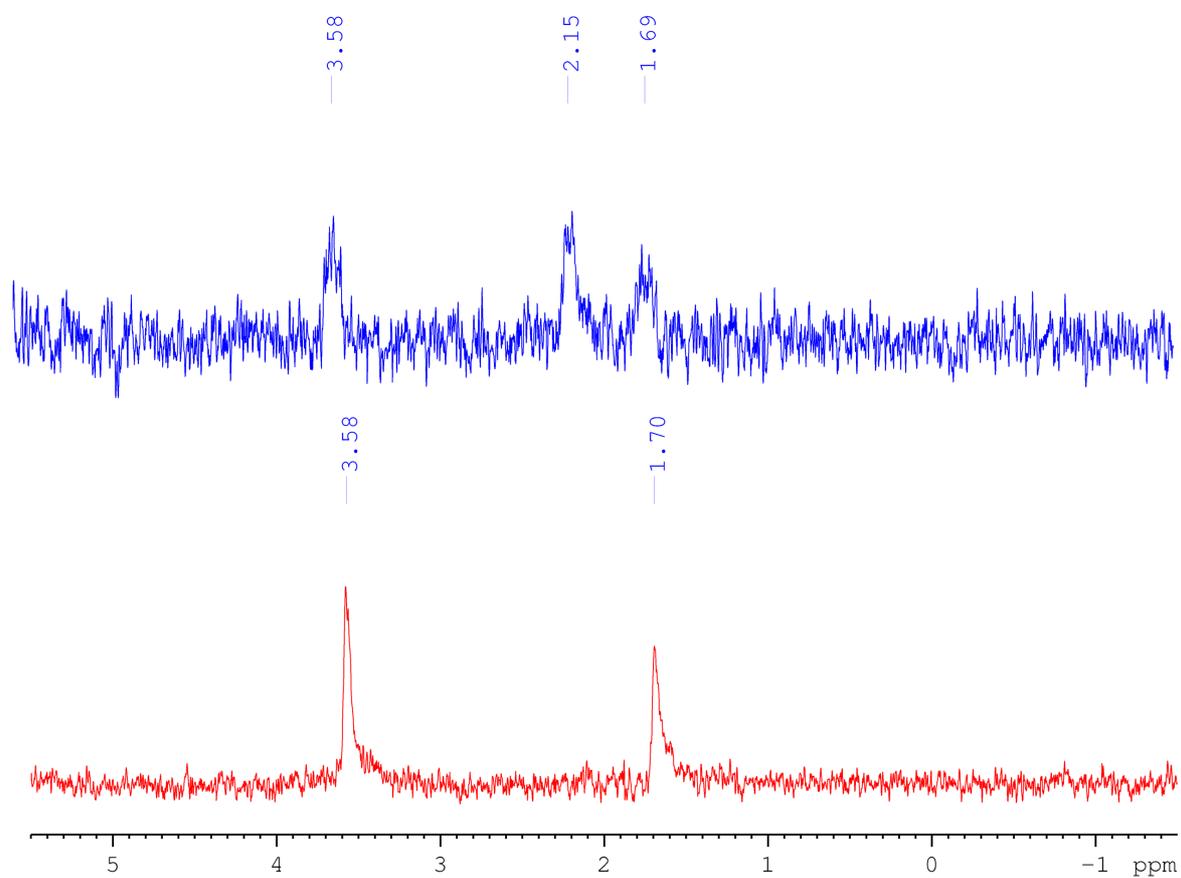
**Figure S6.** Crystal structure of  $[\text{Cr}_2\text{I}(\text{OSi}(\text{O}t\text{Bu})_3)_4]$  (**6a**· $1/2n$ -hexane) along with selected bond lengths (Å). Atomic displacement ellipsoids set at 50% probability. Hydrogen atoms and lattice solvent molecules omitted for clarity. Selected bond angles for **6a**:

atom	atom	atom	angle (°)	atom	atom	atom	angle (°)	atom	atom	atom	angle (°)
Cr2	I1	Cr1	58.731(12)	O5	Cr1	Cr2	44.51(5)	O9	Cr1	Cr2	46.85(5)
Cr2	Cr1	I1	56.652(12)	O9	Cr1	O5	80.37(7)	O9	Cr1	Si2	112.61(5)
Cr2	Cr1	Si2	78.347(19)	O5	Cr1	Si2	34.56(5)	O9	Cr1	O6	148.97(7)
Si2	Cr1	I1	97.852(19)	O5	Cr1	O6	69.59(7)	O6	Cr1	I1	99.54(5)
O5	Cr1	I1	82.12(5)	O9	Cr1	I1	83.42(5)	O6	Cr1	Cr2	109.57(5)

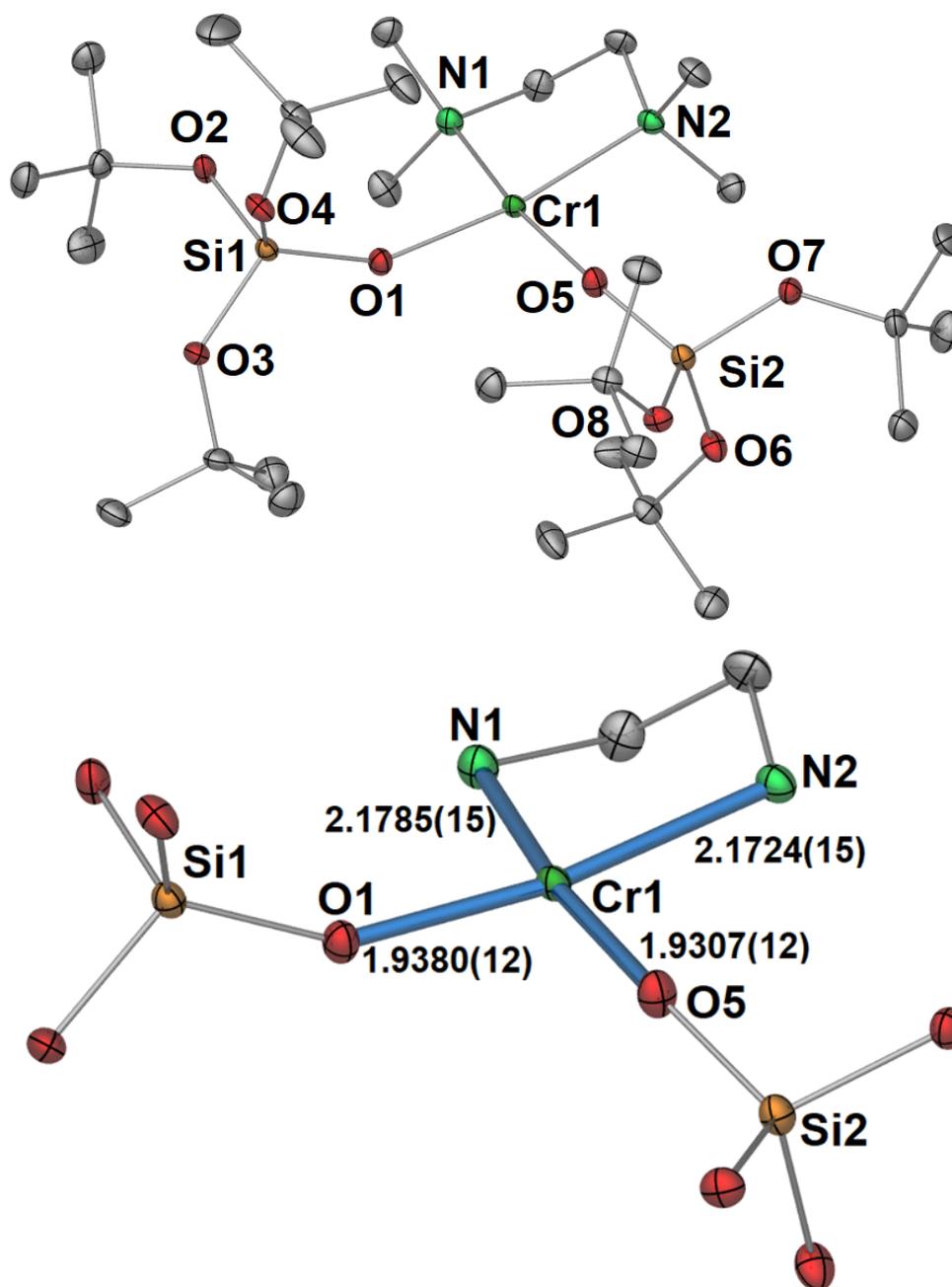


**Figure S7.** Crystal structure of  $[\text{CrCl}_2(\text{tmeda})_2][\text{I}] \cdot \text{THF}$  ( $7 \cdot \text{THF}$ ) along with selected bond lengths (Å). Atomic displacement ellipsoids set at 50% probability. Hydrogen atoms, the second molecule, and lattice solvent molecules omitted for clarity. Selected bond angles for **7**:

atom	atom	atom	angle (°)	atom	atom	atom	angle (°)	atom	atom	atom	angle (°)
Cl2	Cr1	Cl1	180.000(1)	N1	Cr1	N1'	179.4(4)	N2	Cr1	Cl1	90.69(18)
N1	Cr1	Cl1	89.72(18)	N1	Cr1	N2	95.9(2)	N2'	Cr1	Cl1	90.69(18)
N1'	Cr1	Cl1	89.72(18)	N1'	Cr1	N2	84.2(3)	N2	Cr1	Cl2	89.31(18)
N1	Cr1	Cl2	90.28(18)	N1'	Cr1	N2'	95.8(2)	N2'	Cr1	Cl2	89.31(18)
N1'	Cr1	Cl2	90.28(18)	N1	Cr1	N2'	84.2(3)	N2	Cr1	N2'	178.6(4)

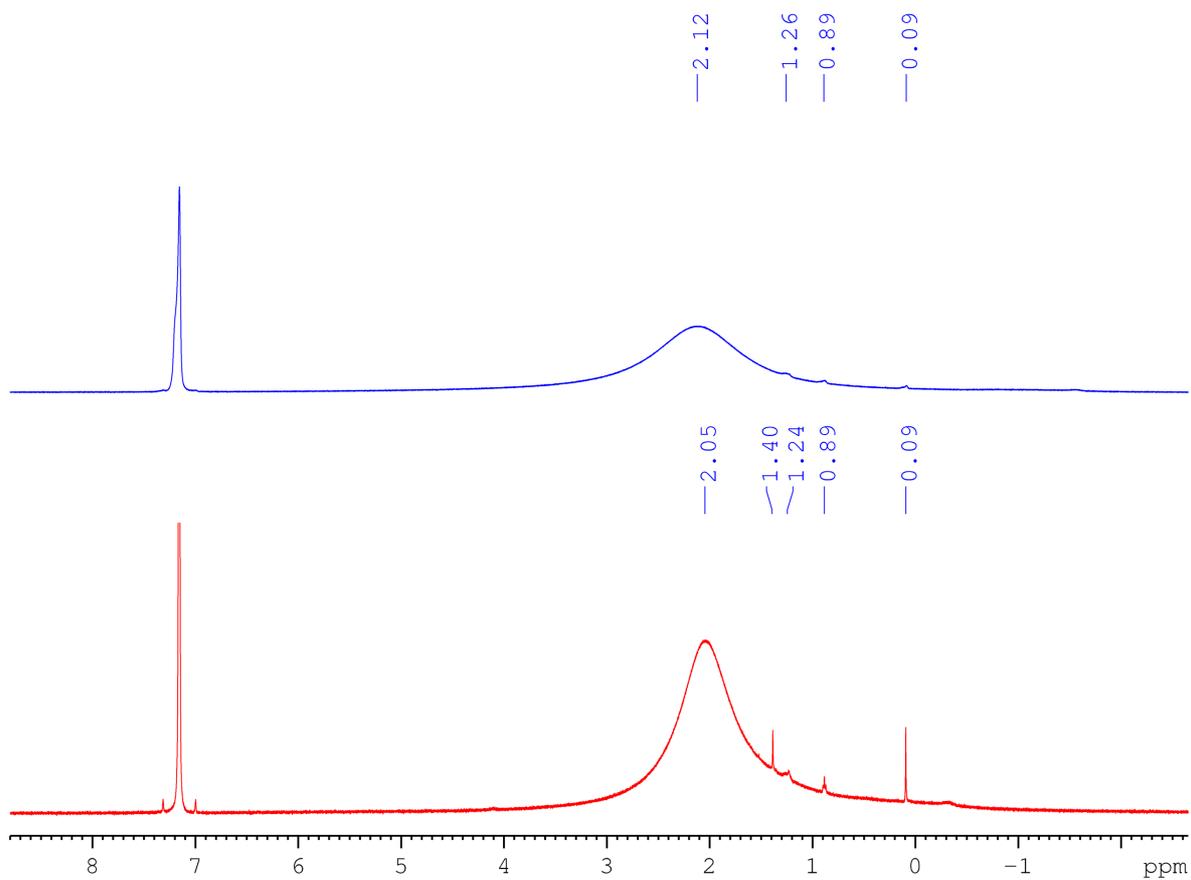


**Figure S8.** Stacked  $^2\text{D}$  NMR spectra (76.77 MHz, 300 K, THF) of the reaction between  $[\text{Cr}_2\text{Cl}_4(\text{CDI})(\text{thf})_{3.5}]$  (**1**) and two equiv of TMEDA. Top: initial measurement, bottom: after approximately 2 h.

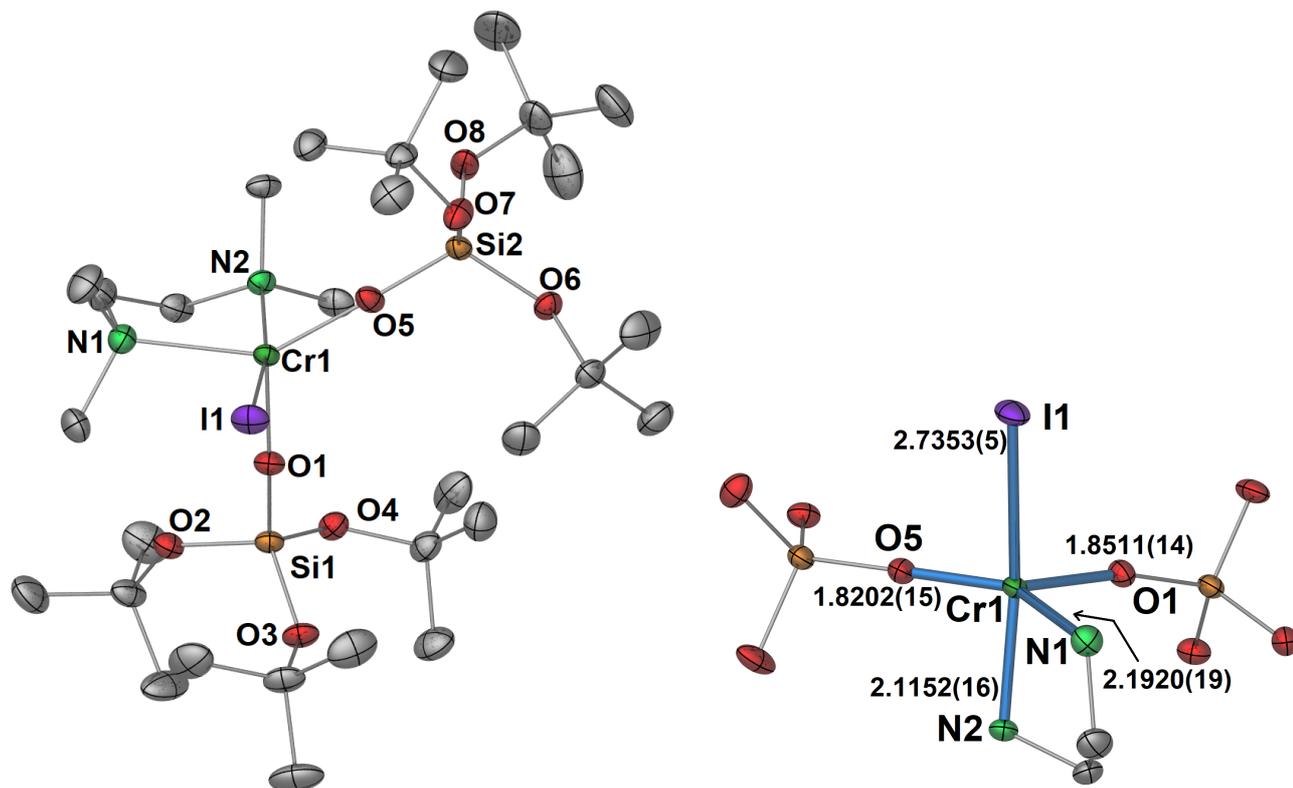


**Figure S9.** Crystal structure of  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2(\text{tmeda})]$  (**8**) along with selected bond lengths (Å). Atomic displacement ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Selected bond angles for **8**:

atom	atom	atom	angle (°)	atom	atom	atom	angle (°)	atom	atom	atom	angle (°)
O1	Cr1	N2	171.09(5)	O1	Si1	O3	116.28(7)	O5	Si2	O8	113.39(7)
O1	Cr1	N1	91.93(5)	O1	Si1	O2	108.63(6)	O5	Si2	O6	115.68(7)
O5	Cr1	O1	97.50(5)	O1	Si1	O4	114.12(7)	O5	Si2	O7	108.64(7)
O5	Cr1	N2	89.83(5)	O3	Si1	O2	106.24(7)	O8	Si2	O7	109.18(7)
O5	Cr1	N1	169.16(6)	O3	Si1	O4	102.39(7)				
N2	Cr1	N1	81.30(5)	O4	Si1	O2	108.65(7)				

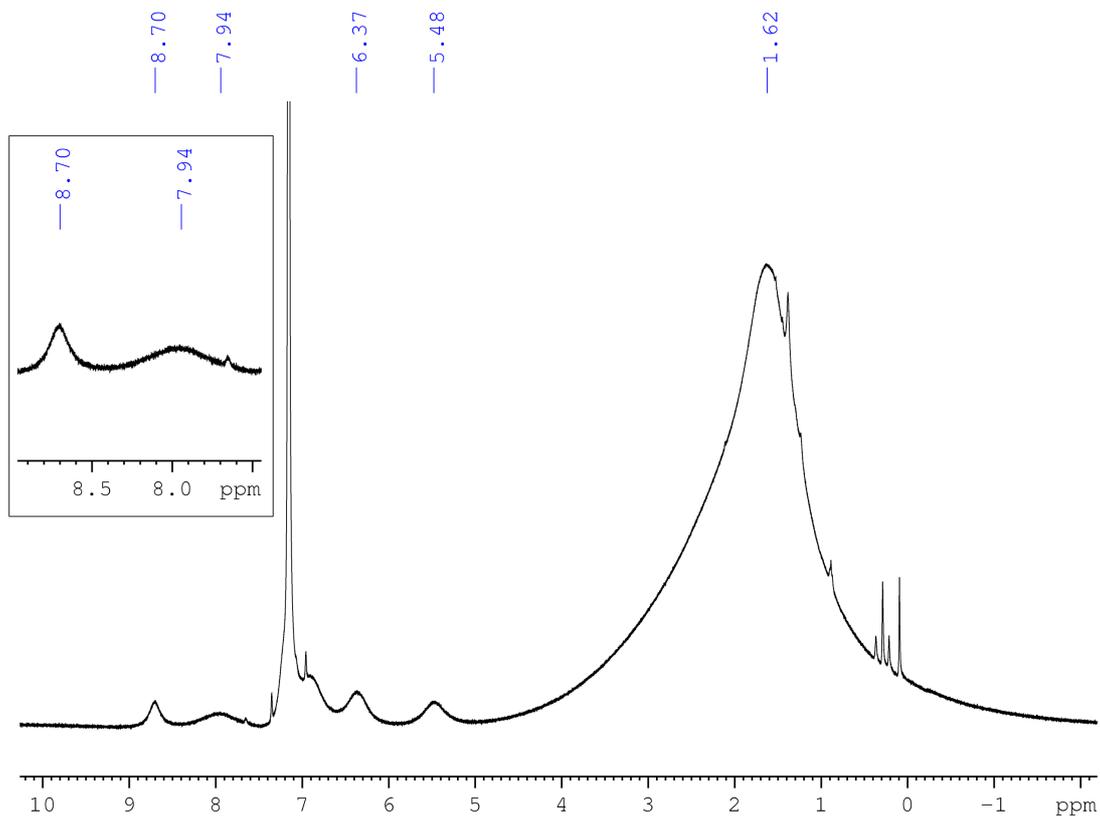


**Figure S10.** Stacked <sup>1</sup>H NMR spectra (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) of [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>(tmeda)] (top, blue), and the reaction between [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>(tmeda)] and CHI<sub>3</sub> in a 2:1 ratio (bottom, red).

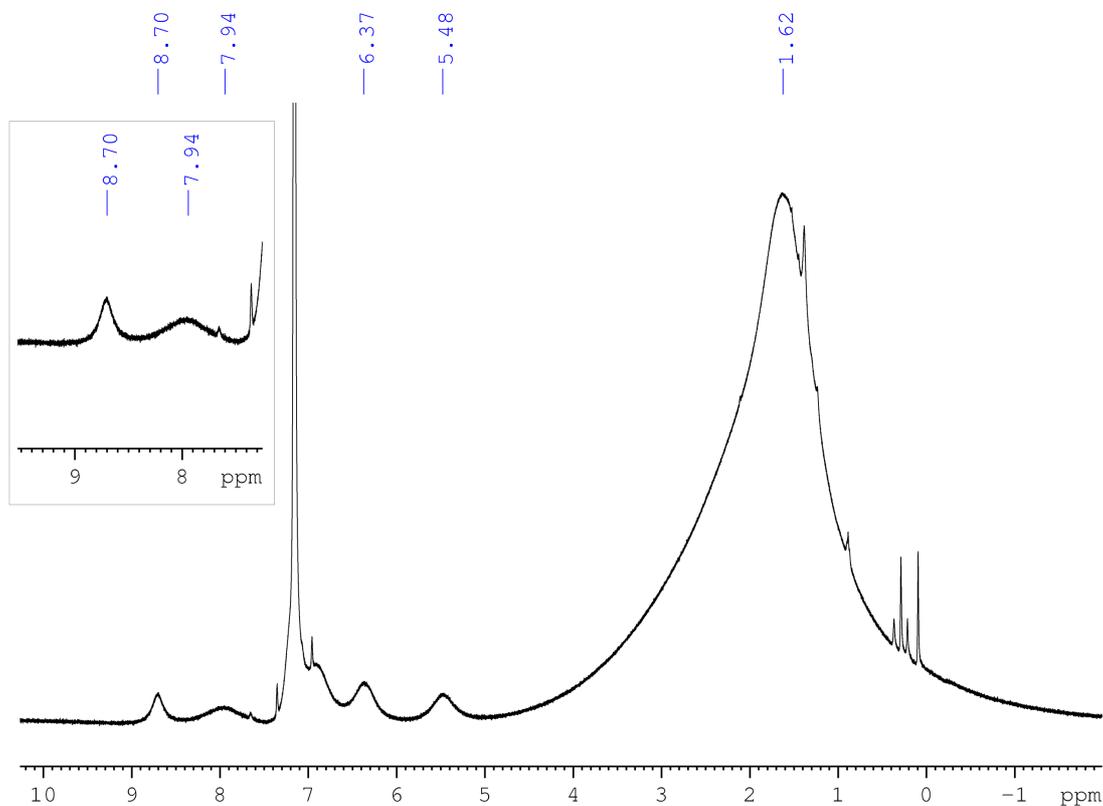


**Figure S11.** Crystal structure of  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2\text{I}(\text{tmeda})] \cdot \frac{1}{2}\text{C}_6\text{D}_6$  ( $10 \cdot \frac{1}{2}\text{C}_6\text{D}_6$ ) along with selected bond lengths (Å). Atomic displacement ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Selected bond angles for **10**:

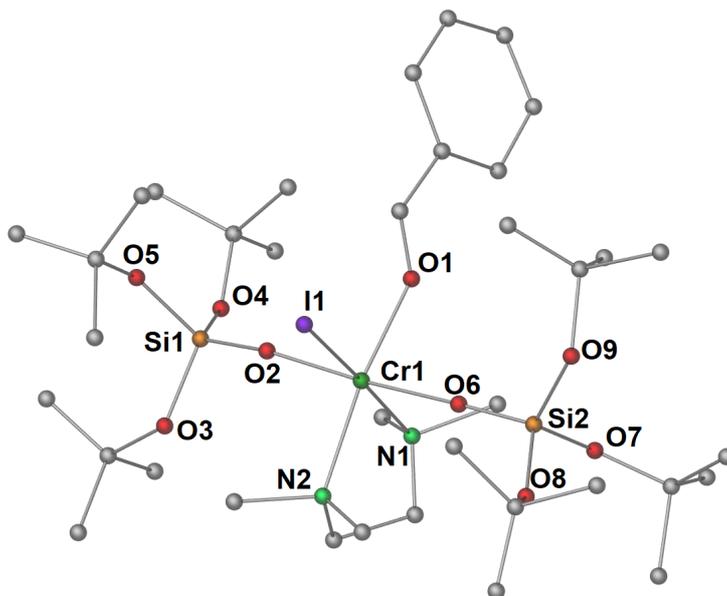
atom	atom	atom	angle (°)	atom	atom	atom	angle (°)	atom	atom	atom	angle (°)
O5	Cr1	I1	91.79(4)	O1	Cr1	I1	96.89(4)	N2	Cr1	I1	167.16(5)
O5	Cr1	O1	119.89(7)	O1	Cr1	N1	95.01(7)	N2	Cr1	N1	80.87(7)
O5	Cr1	N1	144.28(7)	O1	Cr1	N2	93.91(6)	O1	Si1	O2	105.03(8)
O5	Cr1	N2	88.82(6)	N1	Cr1	I1	91.26(5)				



**Figure S12.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) of the reaction between *in situ* generated **9** and benzaldehyde.

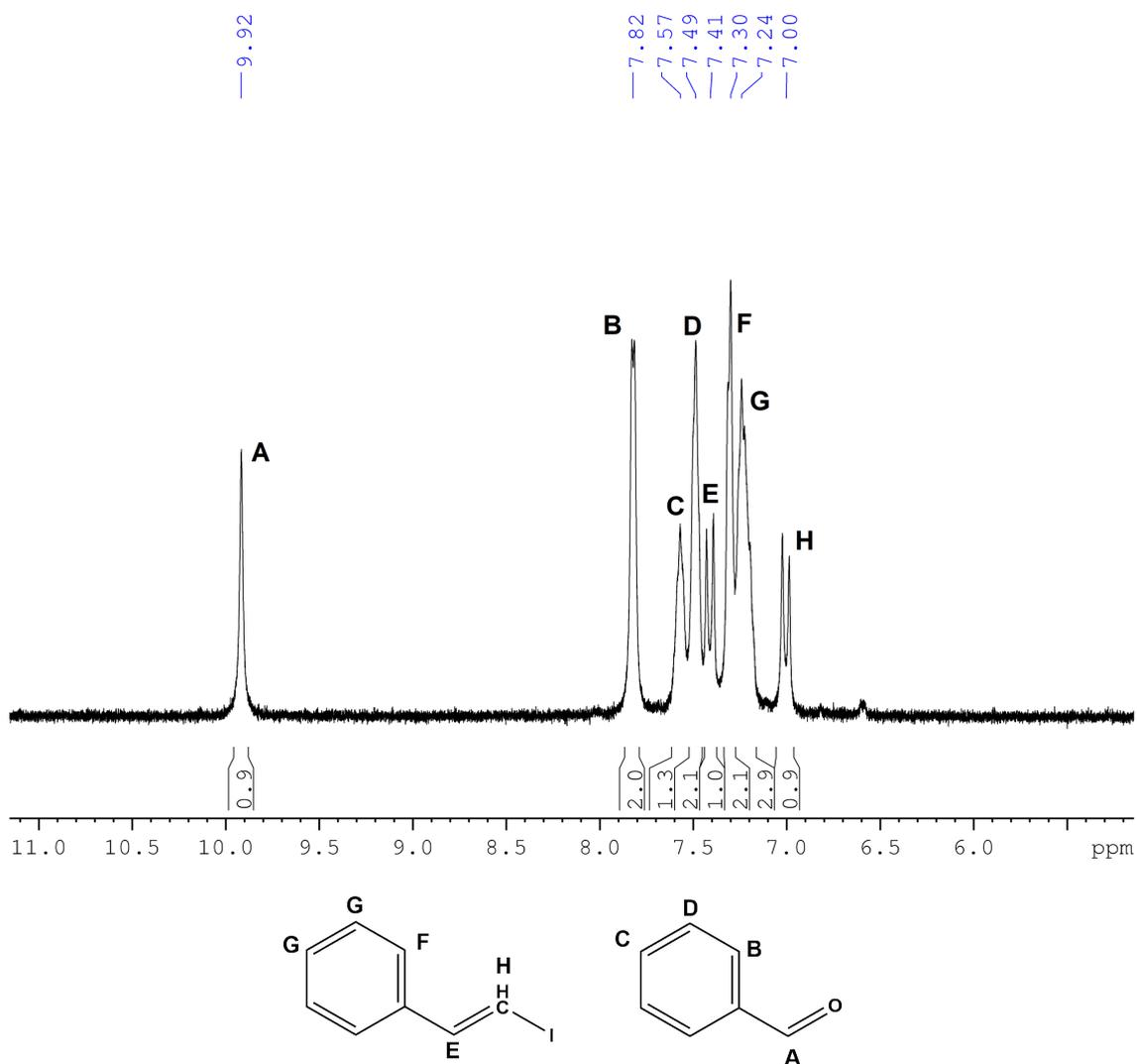


**Figure S13.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) of the reaction between [Cr(OSi(O*t*Bu)<sub>3</sub>)<sub>2</sub>] and benzaldehyde, indicating a degree of coordination to the paramagnetic chromium center.

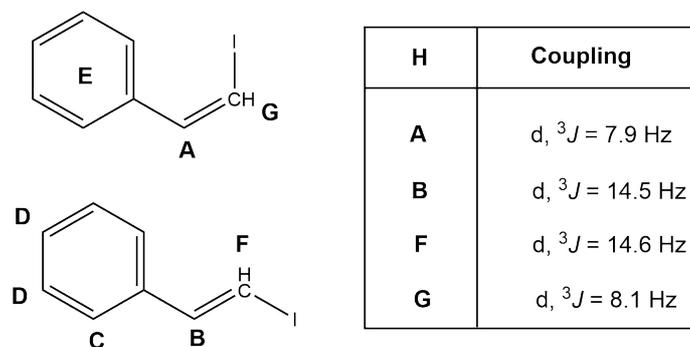
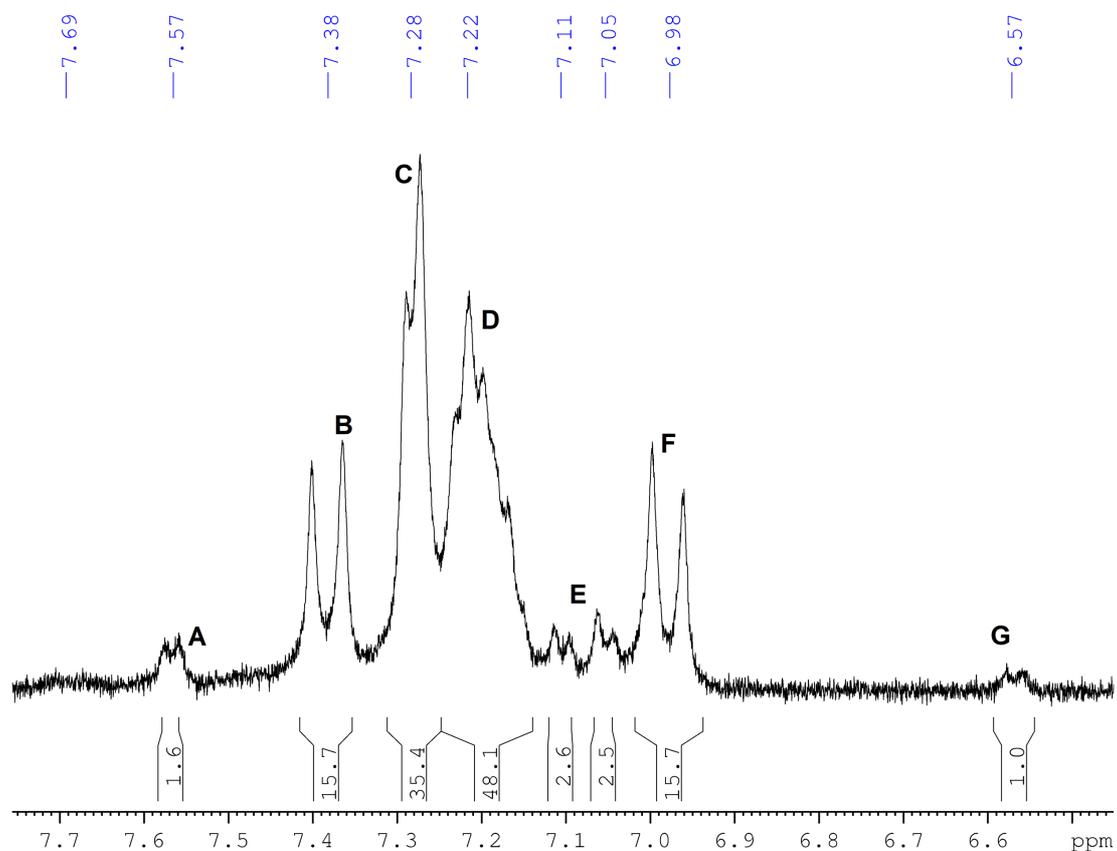


**Figure S14.** Connectivity structure of  $[\text{Cr}(\text{OSi}(\text{O}t\text{Bu})_3)_2\text{I}(\text{benzaldehyde})] \cdot \text{C}_6\text{D}_6$  (**11**). The crystals were highly twinned and the asymmetric unit contained four molecules; the atoms could not be refined anisotropically, hence bond lengths and angles are not reported. Unit cell:  $a = 28.881(3) \text{ \AA}$ ,  $b = 9.4971(10) \text{ \AA}$ ,  $c = 76.031(8) \text{ \AA}$ ,  $\beta = 92.293(2)^\circ$ .

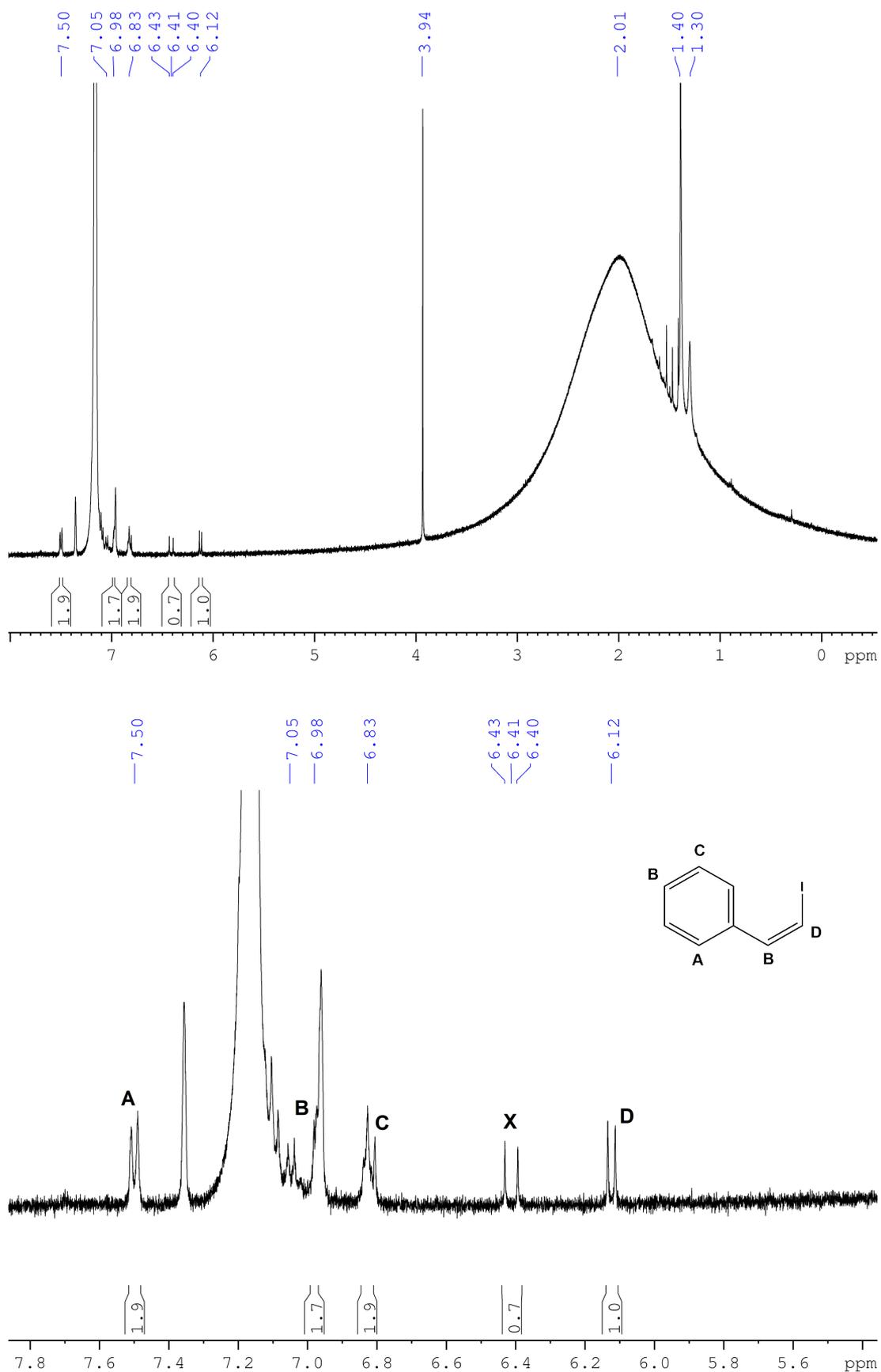
## Additional Relevant Spectra



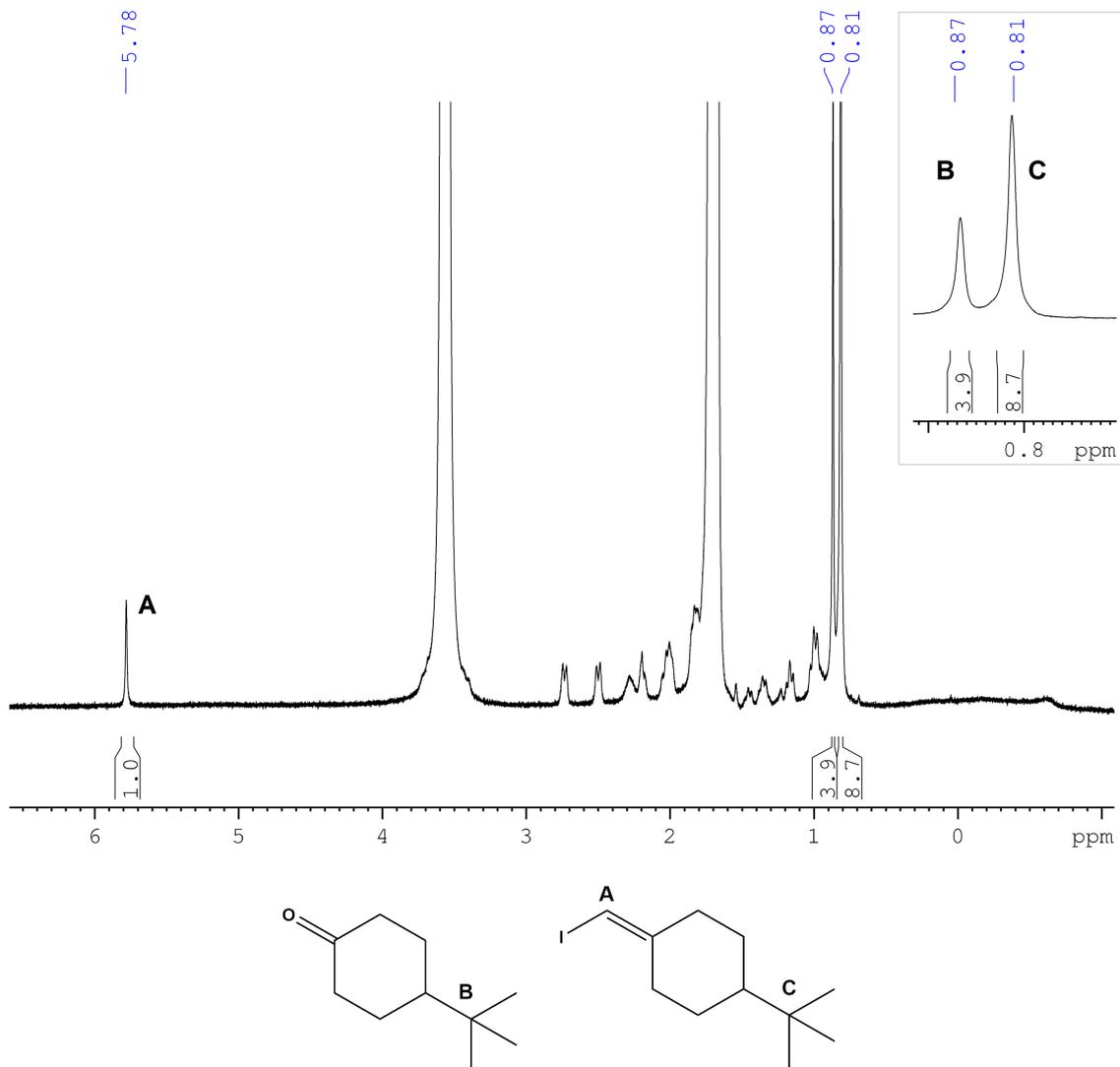
**Figure S15.** <sup>1</sup>H NMR spectrum (400 MHz, THF-d<sub>8</sub>, 300 K) of the reaction between CrCl<sub>2</sub>, iodoform, and benzaldehyde in a ratio of 4:1:1, after filtration from insoluble species.



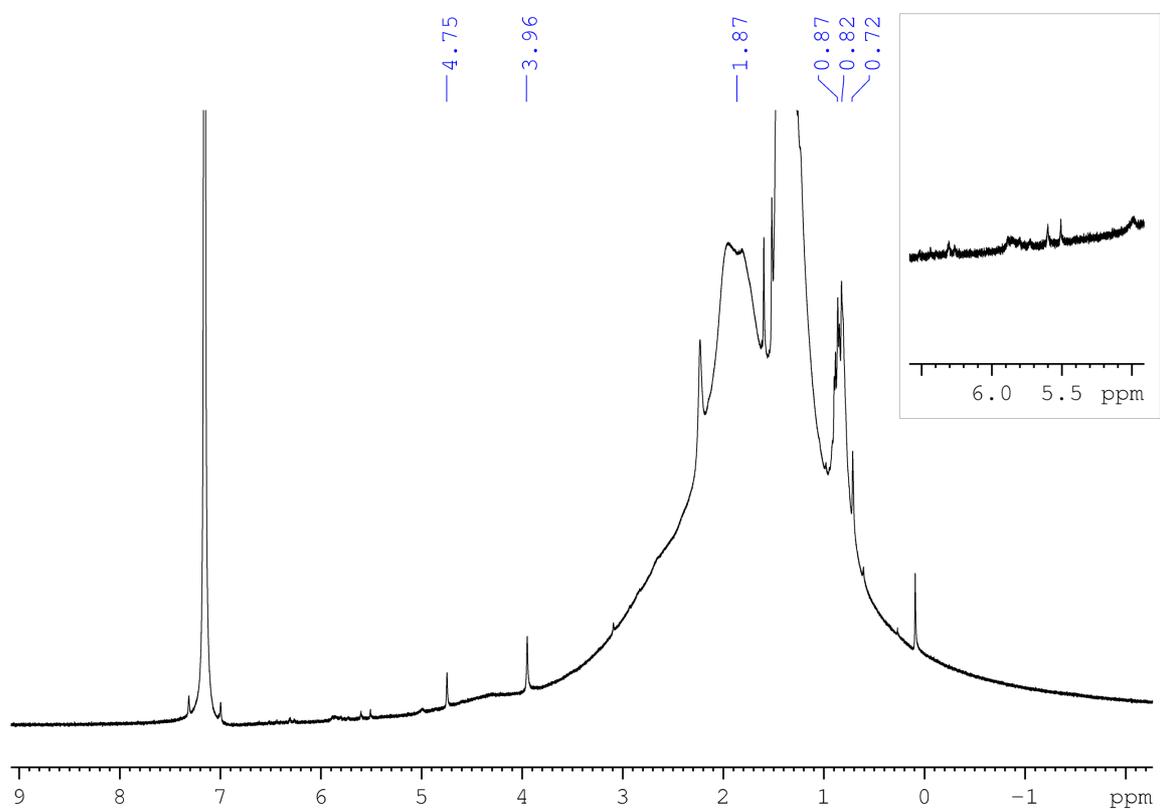
**Figure S16.** <sup>1</sup>H NMR spectrum (400 MHz, THF-d<sub>8</sub>, 300 K) of the reaction between **1** and half an equiv of benzaldehyde, after filtration from insoluble species.



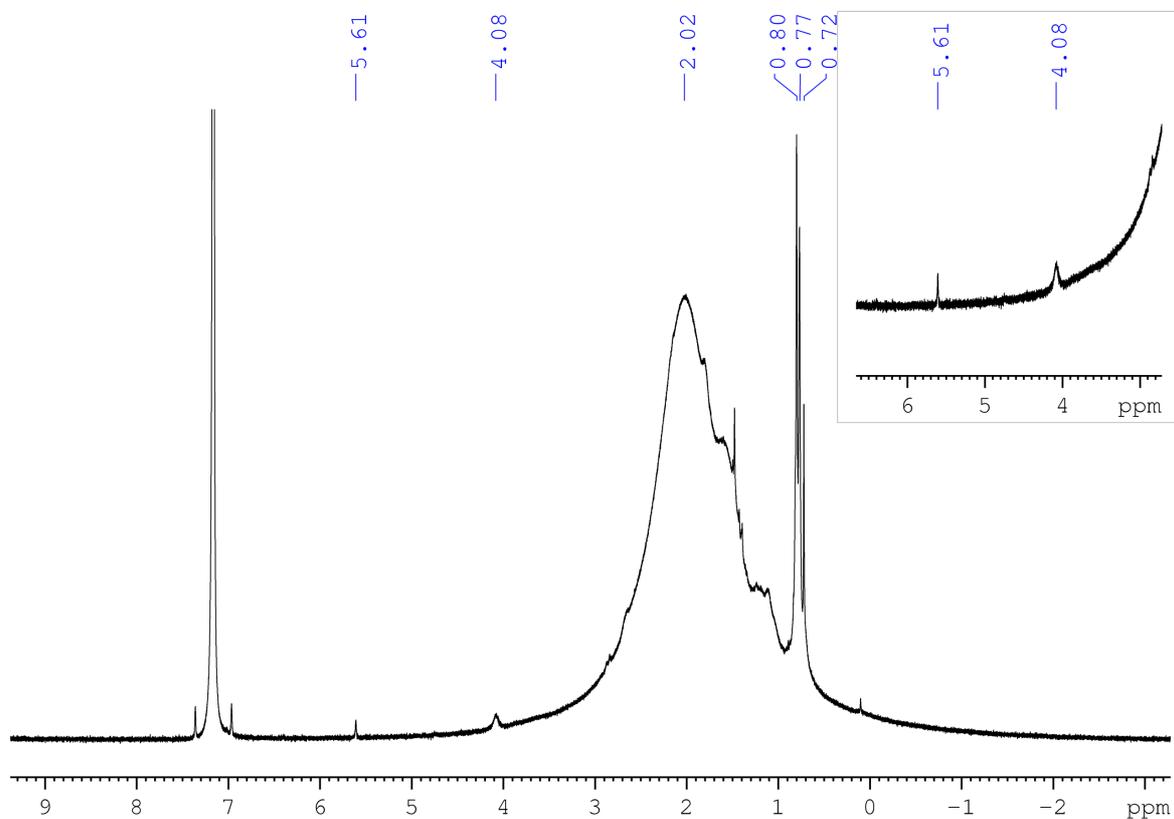
**Figure S17.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) of the reaction between *in situ* generated **5a** and half an equiv of benzaldehyde, giving (E/Z)-(2-iodovinyl)benzene in a ratio of ca. 40 (X):60 (Z). Resonances X and D disappeared when the reaction was performed using *in situ* generated **5a<sup>D</sup>**. Top: entire spectrum; bottom: selected range.



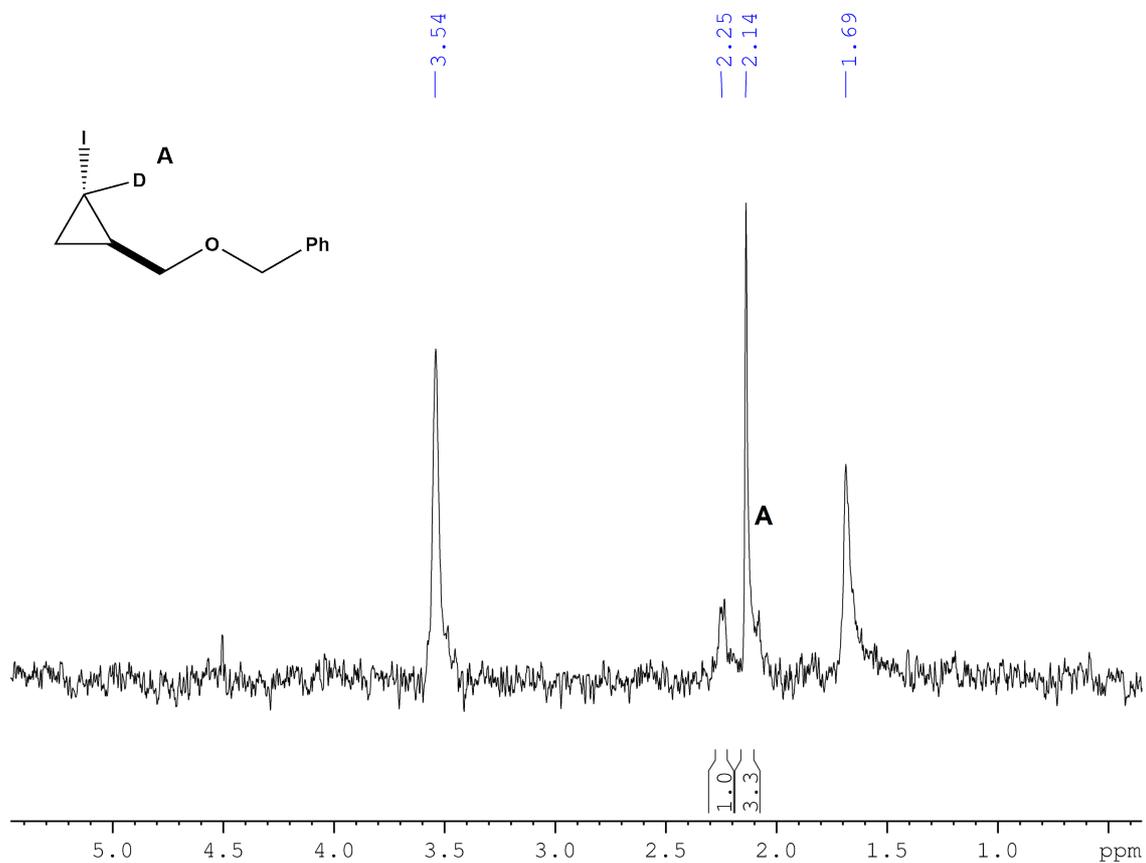
**Figure S18.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{THF-d}_8$ , 300 K) of the reaction between **1** and one equiv of 4-*tert*-butylcyclohexanone. Heating this reaction mixture at 50 °C for 10 min changed the ratio of obtained products.



**Figure S19.** <sup>1</sup>H NMR spectrum (500 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) of the reaction between *in situ* generated **5a** and 4-*tert*-butylcyclohexanone. Heating this reaction mixture at 50 °C caused decomposition as indicated by the appearance of additional peaks in the spectrum.



**Figure S20.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ , 300 K) of the reaction between *in situ* generated **9** and 4-*tert*-butylcyclohexanone. Examination of the reaction mixture, after separation of crystalline **9** and **10**, as new resonances were observed within the spectrum.



**Figure S21.** <sup>2</sup>D NMR spectrum (77 MHz, THF, 300 K) of  $[\text{Cr}_2\text{Cl}_4(\text{CDI})(\text{thf})_4]$  (**1<sup>D</sup>**) in the presence of two equiv of TMEDA and one equivalent of allyl benzyl ether, indicating the presence of the *trans* isomer.

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